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JANUARY, 1929

Theory of the Stark Effect in Hydrogenic Atoms — Vladimir Rojansky 1

[illegible] of Beryllium — R. F. Paton and G. M. Kalmykow 16

[illegible] of the Life of the [illegible] Mercury Atom — M. L. Eaton 23

[illegible] of C-H and [illegible] Vibration Spectra — Joseph W. Ellis 37

[illegible] of Certain Compounds in the Near Infra-Red — James W. Shrum 57

[illegible] Diamagnetism of the [illegible] Metals of Group — E. E. Burton 45

[illegible] Cathode Current [illegible] — J. Slepian and E. J. Shaughnessy 52

[illegible] as a Dielectric [illegible] Corona Current. II. The Effect of [illegible] and of Temperature upon the [illegible] — Lovell S. McDaniel and Elisha L. Thompson 65

[illegible] Dorbine and [illegible] in Silver and Brass — K. M. Irwin and H. M. [illegible] 68

[illegible] Current on the [illegible] Wire — [illegible] 78

[illegible] of the [illegible] Proposals by the Committee — [illegible] 86

[illegible] Measurements [illegible] of Sound in Gases — A. B. [illegible] and E. L. [illegible] 89

[illegible] Shock — J. [illegible] 98

[illegible] — [illegible] 108

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

[illegible] Meeting, November [illegible] — [illegible] 113

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THE

PHYSICAL REVIEW

ON THE THEORY OF THE STARK EFFECT IN HYDROGENIC[1] ATOMS.[2]

By Vladimir Rojansky

Abstract

The Stark effect of the fine structure of hydrogenic atoms is discussed in the light of the quantum mechanics. Explicit formulas are given for the energy levels in either a weak or a strong electric field, including in each case both the relativity corrections and the Stark effect. (The conventional treatment neglects either one or the other.) The results are, except in form, similar to those recently given by Schlapp. In the new mechanics, in contradistinction to the old Bohr theory, there is a linear Stark effect even in weak fields, because of the identity of energy for the ns and np_1 levels in the absence of external fields. This degeneracy is shown to account for the results of the recent experiments of Ornstein, Zernike, and Snoek, who found that the $2s$ level in H is not metastable.

The coefficients are found for the development of the "parabolic" eigenfunctions in terms of the "polar" ones, and a set of numerical values of these coefficients is tabulated.

Methods are given for the calculation of the relative intensities in the Stark effect in terms of the already available theoretical fine structure intensities in the absence of fields.

I. Energy Levels

1. *Introduction.* By the time the present investigation was begun several important expressions relative to the energy levels of hydrogenic atoms perturbed by an homogeneous and constant external electric field had been derived on the basis of the new quantum mechanics. In the first place, the formula[3] $-e^2Z^2/2a_1n^2$ of the Bohr theory for the energy levels of an unpertured Newtonian hydrogenic atom, without spin, had been verified. It had also been shown by Heisenberg and Jordan[4] that the relativity-and-spin corrections for the energy levels are given, to terms of the order of $1/c^2$, by

$$\frac{16\Delta W_H Z^4}{n^3}\left(\frac{3}{4n}-\frac{1}{j+\frac{1}{2}}\right). \tag{1}$$

[1] By an hydrogenic atom we mean an atom consisting of a nucleus of net charge Ze, and of one electron of charge $-e$.

[2] A summary of the parts of this paper relative to the linear effect in weak fields and to the metastability of the state $2s$ in H was given in the program of the June, 1928, meeting of the American Physical Society, Phys. Rev., **32**, 327 (1928).

[3] In this paper all formulas are written in a uniform notation explained in Section 2.

[4] W. Heisenberg and P. Jordan, Zeits. f. Physik, **37**, 263 (1926).

The fact that the azimuthal quantum number does not appear in this formula shows that the system consisting of a relativistic hydrogenic atom with a spinning electron is, in the absence of an external field, degenerate with respect to the azimuthal quantum number, at least to this degree of approximation. It was later shown by Darwin and by Gordon[5] that, with the Dirac's "quantum theory of the electron," the exact expression for the energy also reveals this degeneracy. Formula (1) represents the relativity-and-spin corrections also for the case in which the atom is perturbed by a weak external field, i.e., a field whose perturbing influence is small compared to that of relativity and spin in the absence of a field.

For the case in which the atom is perturbed by a strong external electric field, i.e., a field whose perturbing influence is great compared to that of relativity and spin in the absence of a field, it had been found[6 7 8] that the energy levels of a Newtonian hydrogenic atom, without spin, are given, to terms in F^2, by

$$-\frac{e^2Z^2}{2a_1n^2}-\frac{3a_1eFnn_F}{2Z}-\frac{\alpha^2a_1^2e^2F^2}{512\Delta W_HZ^4}n^4(17n^2-3n_F^2-9m_l^2+19). \qquad (2)$$

It was therefore thought advisable to investigate, as the main purpose of the present paper, the terms depending on F for the case of *weak* fields, and the relativity and spin correction for the case of *strong* fields, since the conventional formulas (1) and (2) give the latter only in weak, and the former only in strong fields.

However, before this work was completed, there appeared a paper by Dr. Schlapp,[9] in which he investigated, in a very elegant fashion, the nature of the Stark effect in hydrogenic atoms from the standpoint of the Darwin-Dirac theory, and considered in particular the limiting cases of a weak and of a strong electric field. With regard to the energy levels he gave a procedure for finding the energy of any quantum state, gave a method for correlating the weak field and the strong field levels, and worked out in detail the three lower sets of energy levels in hydrogen for both a weak and a strong field. With regard to intensities he gave a procedure for calculating them, and considered in detail the components of H_α. One of the most interesting results found by Schlapp is the presence of linear Stark effect in weak fields, a phenomenon peculiar to the new quantum theory and contradictory to that of Bohr.[10] Schlapp suggests that study of the polarization of the spectral

[5] C. G. Darwin, Proc. Roy. Soc., **118A**, 654 (1928); W. Gordon, Zeits. f. Physik, **48**, 11 (1928).

[6] W. Pauli, Zeits. f. Physik, **36**, 336 (1926); term in F. G. Wentzel, Zeits. f. Physik, **38**, 518 (1926), and P. S. Epstein, Phys. Rev., **28**, 695 (1926); terms in F and F^2.

[7] E. Schroedinger, Ann. d. Physik, **80**, 437 (1926); term in F.

[8] I. Waller, Zeits. f. Physik, **38**, 635 (1926); terms in F and F^2.

[9] R. Schlapp, Proc. Roy. Soc., **119A**, 313 (1928). We may add here that we shall not attempt to discuss the adiabatic correlation of levels in weak and strong fields, embodied in our Eqs. (22 *a*, *b*). This can be handled by the principle of the "non-crossing-over" of the energy values, and is thoroughly discussed by Schlapp.

[10] H. A. Kramers, Zeits. f. Physik **3**, 199 (1920).

lines might be more successful in testing this conclusion experimentally than attempts to resolve the components.

While the methods used by Schlapp are much more elegant, mathematically, than ours, we believe that our final results appear in a form which is easier to handle in calculation, as it is explicit. The present paper, which does not use the Dirac's theory, also makes the results easier to visualize, as the different types of quantization of the spin axis appropriate to various fields are clearly exhibited rather than shrouded in the equations.

2. *Terminology and notation.* In the study of an hydrogenic atom, without spin, perturbed by a weak external field, the appropriate equations are set up in spherical polar coordinates, and it is found that the quantum states of the atom can be identified with sets of quantum numbers n,l, and m_l. Here n $(=1, 2, \cdots)$ and l $(=0, 1, \cdots, n-1)$ are respectively the principal and the azimuthal quantum numbers. The latter measures the orbital angular momentum in terms of the quantum unit $h/2\pi$, and is, for any given quantum state, one unit lower than the quantum number k of the older theory. The quantum number m_l $(=-l, \cdots, l)$ specifies, in the same units, the component of the orbital angular momentum in the direction of the external field.

To include the effect of spin the angular momentum due to the rotation of the electron about its own axis must be introduced. This leads to the appearance of the additional quantum numbers s, m_s, j, and m. The numbers of the resulting set are not all independent. The spin quantum number s equals $1/2$ for doublet spectra, i.e., for the spectra of hydrogenic atoms and of alkalis, and determines the spin angular momentum. The resultant angular momentum of the atom is measured by the inner quantum number j, which for doublet spectra equals $l \pm 1/2$. The quantum numbers m_s and m are related to s and j, respectively, in the same way as m_l is related to l. It follows that $m = m_l + m_s$. Here m is called the axial, or magnetic quantum number. When spin is neglected s and m_s can both be regarded as zero.

When an hydrogenic atom is perturbed by a strong external electric field the situation changes to such an extent that in setting up the equations it is convenient to use the parabolic system of coordinates. This leads to the appearance of a new set of quantum numbers which we denote by n, m, m_l, m_s, s, p, and n_F, and which are not all independent. The first five of these can be identified with those similarly denoted and described above. In the present paper we neglect the slight interaction between the orbital and the spin angular momenta in their nearly uncoupled precessions about the direction of the strong external field, and therefore regard m_l and m_s as constant for any given quantum state. The integer p, such that $0 \leqq p \leqq n - |m_l| - 1$, we call the parabolic quantum number. Its physical significance lies in the fact that the expression $n(n - 2p - |m_l| - 1)$ measures, in units $3h^2/8\pi^2 Zem$, the average value of the electric moment of the atom in the direction of the external electric field. We set $n - 2p - |m_l| - 1 = n_F$, and call the integer n_F the electric quantum number.

To shift to this notation from the usual notation originated by Epstein, we substitute our expressions n, p, $n-p-|m_l|-1$, $|m_l|+1$, and $-n_F$, respectively, for n, n_1, n_2, n_3, and n_F. To shift from that of Schroedinger,[7] we substitute our expressions n, p, $n-p-|m_l|-1$, $|m_l|$, and n_F, respectively, for l, k_1, k_2, n, and k^*.

In addition to the symbols described above, and the usual e,h,c, and[1] Z, we use: m for the mass of an electron;[11] $a_1(=h^2/4\pi^2me^2)$ for the radius of the first Bohr orbit in hydrogen; $\alpha(=2\pi e^2/ch)$ for the Sommerfeld's fine structure constant; $\Delta\nu_H$ $(=\pi^4me^8/2c^3h^5)$ for the separation, in wave-numbers, of the two $n=2$ levels in a relativistic hydrogen atom with a spinning electron; ΔW_H $(=\Delta\nu_H ch)$ for the energy difference corresponding to the wave-number separation $\Delta\nu_H$; F for the strength of an external electric field measured in e.s.u. of potential per cm.; and m^* for $|m_l|$.

3. *The case of a weak electric field.* In this case we shall consider the unpertured system to consist of a relativistic hydrogenic atom with a spinning electron, and shall evaluate, by means of the matrix perturbation theory, the perturbations of energy produced by the external electric field. Accordingly, we shall seek to find the elements of the matrix representing the Hamiltonian of the perturbed system in order that the energy of the quantum states could be found, to terms in F^2, by means of the formulas:[12]

$$W^{(1)}(k\,;k)=H^{(1)}(k\,;k)\;;\; W^{(2)}(k\,;k)=H^{(2)}(k\,;k)+\sum_{k'}{}'\frac{H^1(k\,;k')H^1(k'\,;k)}{h\nu_0(k\,;k')}\cdot \quad (3)$$

Here k is the totality of the quantum numbers defining a state, and $\nu_o(k;k')$ is the transition frequency of the unperturbed system, to be evaluated, in our case, by (1).

The external electric field of strength F is here assumed to be directed along the z-axis of the coordinate system, so that the perturbing potential is given by the matrix representing Fez. We shall therefore first consider the elements of the z-coordinate matrix. It will be recalled that these elements are diagonal in the axial quantum number. We shall restrict ourselves to elements which are also diagonal in n. The reason for this is that non-diagonal elements are to be used only in the second formula of (3), and that for elements non-diagonal in n the frequencies in the demoninators are so large that it is not necessary to consider the terms involving them. (Such high frequency terms are, however, responsible for the F^2 term of the formula (2) for strong fields.)

We begin by considering the elements of the x-, y-, and z-coordinate matrices for the case of a strong magnetic field. Here the spin is quantized separately, so that the elements can be found by means of the relations[13] for the evaluation of matrix elements by the use of wave mechanics. For the elements of the coordinate matrices these relations are

[11] We do not discriminate here between the rest mass and the reduced mass $m_{el}m_{nu}/(m_{el}+m_{nu})$ of the electron.

[12] M. Born, W. Heisenberg, and P. Jordan, Zeits. f. Physik, **35**, 557 (1926).

[13] E. Schroedinger, Ann. d. Physik, **79**, 734 (1926); C. Eckart, Phys. Rev., **28**, 711 (1926).

$$q_i(n,m_l,l\ ;n',m_l',l') = \iiint \Psi^*(n,m_l,l)\, i\, \Psi(n',m_l',l')\, dv. \qquad (4)$$

Here i is x, y, or z, Ψ is the Schroedinger's eigenfunction (5), and Ψ^* is its complex conjugate. The integration is to be extended over all space.

To introduce the effect of spin into the q's calculated from (4), we consider the intensities of transitions, which are proportional to the squares of the corresponding q's, and apply the Burger-Dorgelo-Sommerfeld sum rule.[14] After this the effect of spacial quantization is introduced by means of the proper Kronig's factors.[15] The expressions so obtained are intensities in the presence of spin and of a weak external field, and from these we go back to q's. Eliminating l by the relation $l=j\pm 1/2$, suppressing among the indices the quantum numbers n and m, which remain constant in the transitions of interest to us, writing the remaining quantum numbers in the order l, j, and using the abbreviations:

$$K(j) = -3a_1 n(j^2-m^2)^{1/2}/8Zj, \qquad L(j) = [n^2-(j+\tfrac{1}{2})^2]^{1/2},$$
$$M = -3a_1 n\{[n^2-(j+\tfrac{1}{2})^2]m^2\}^{1/2}/4Zj(j+1),$$

we can write the resulting elements of the matrix $\boldsymbol{q}_z$ in the form:

$$q_z(j+\tfrac{1}{2},j\ ;j-\tfrac{1}{2},j-1) = 2K(j)L(j)\ ; \qquad q_z(j+\tfrac{1}{2},j\ ;j+\tfrac{3}{2},j+1) = 2K(j+1)L(j+1);$$
$$q_z(j-\tfrac{1}{2},j\ ;j-\tfrac{3}{2},j-1) = 2K(i)L(i-1)\ ;\ q_z(j-\tfrac{1}{2},j\ ;j+\tfrac{1}{2},j+1) = 2K(j+1)L(j)\ ;$$
$$q_z(i+\tfrac{1}{2},j\ ;j-\tfrac{1}{2},j) = q_z(j-\tfrac{1}{2},j\ ;j+\tfrac{1}{2},j) = M$$

The off-diagonal elements of the matrix $\boldsymbol{H}$ representing the Hamiltonian of the perturbed system can be obtained from these by using the multiplier Fe. The diagonal elements of $\boldsymbol{H}$ are given by the sum of $-e^2Z^2/2a_1\, n^2$ and of (1).

Formulas (3) cannot be applied directly to $\boldsymbol{H}$ since the transition frequencies corresponding to elements non-diagonal in l but diagonal in j vanish due to the degeneracy of the unperturbed system. This indicates that the canonically conjugate coordinates and momenta implied in our problem need to be transformed, and that we must seek a canonical matrix transformation which will shift the troublesome off-diagonal terms onto the diagonal of the matrix representing the Hamiltonian. Consideration of just the interaction between the pair of elements $j=l\pm\frac{1}{2}$, which can be conveniently treated by making the corresponding energy determinant vanish, leads to the transformation matrix $\boldsymbol{S}$, whose elements are:
for $j<n-\frac{1}{2}$:

$$S(j-\tfrac{1}{2},j\ ;j+\tfrac{1}{2},j) = S(i-\tfrac{1}{2},j\ ;j-\tfrac{1}{2},j)$$
$$= S(j+\tfrac{1}{2},j\ ;j+\tfrac{1}{2},j) = -S(j+\tfrac{1}{2},j\ ;j-\tfrac{1}{2},j) = (2)^{-1/2}$$

[14] A. Sommerfeld, *Atombau*, 4th Ed., Chap. VIII, §5. Note that when spin is introduced in our case the total a priori probability is doubled.

[15] S. Goudsmit and R. de L. Kronig, Amsterdam Akad. Proc., **28**, 418 (1925); R. de L. Kronig, Zeits. f. Physik, **31**, 885 (1925); H. Hönl, Zeits. f. Physik, **31**, 340 (1925).

for $j=n-\frac{1}{2}$: $\quad S(n-1, n-\frac{1}{2}; n-1, n-\frac{1}{2})=1$

We now apply the perturbation formulas (3) to the transformed Hamiltonian $\boldsymbol{H}_1=\boldsymbol{S}\boldsymbol{H}\tilde{\boldsymbol{S}}^*$. We find that in $W(j-\frac{1}{2},j)$ and $W(j+\frac{1}{2},j)$ the terms linear in F have the same absolute value, but differ in sign. Both expressions can be combined into one by introducing the factor $2(l-j)$, which is $+1$ when $l=j+\frac{1}{2}$, and -1 when $l=j-\frac{1}{2}$. In this manner we obtain Eq. (14) of Section 8. The appearance of l in this equation means that a weak external electric field removes the degeneracy of the unperturbed system with regard to this quantum number: the levels $(j-\frac{1}{2},j)$ and $(j+\frac{1}{2},j)$, which coincide in the unperturbed atom, are separated by the external field, and the separation is proportional to the field. Application of the second formula of (3) to $\boldsymbol{H}_1$ gives Eqs. (15*a*) and (15*b*).

4. *The case of a strong electric field. Outline of procedure.* In this case we shall designate as the *unperturbed* system the system consisting of a Newtonian hydrogenic atom, without spin, acted on by a strong external electric field F. The energy of this system is given, to terms in F^2, by (2). In accordance with our definition of a strong external field, the effects of relativity and of spin cause small perturbations in this system. To evaluate the energy of the perturbed system we resort to the theorem which states that the energy of a perturbed system is to a first approximation equal to the energy of the unperturbed system plus the perturbing potential averaged over the unperturbed system. In the matrix mechanics this theorem is expressed by the first formula of (3).

This problem is very similar to that, solved by Heisenberg and Jordan,[4] of finding the relativity and the spin corrections for an hydrogenic atom in the absence of an external field. The only difference between the two problems is that the effects of relativity and of spin must be averaged over different unperturbed systems. We shall seek a procedure which will enable us to express the averages needed in our case in terms of the averages occurring in Heisenberg and Jordan's problem. This can be accomplished by the study of a certain linear relation between the Schroedinger's eigenfunctions appropriate to the two cases. Our final formulas for the relativity and the spin corrections in strong fields are essentially summations of the corrections given by Heisenberg and Jordan.

5. *Linear dependence of eigenfunctions.* When the wave mechanics is used in connection with the problem of an unperturbed Newtonian hydrogenic atom, without spin, the Schroedinger's eigenfunctions are found by solving his amplitude equation expressed in spherical polar coordinates. This leads to a system of solutions[7,8] which, with the abbreviations $\xi=Zr/na_1$, $\mu=\cos\theta$, $m^*=|m_l|$, can be written as[16]:

$$\Psi=\left\{\frac{2^{2l}Z^3[2l+1](l-m^*)!\,(n-l-1)!}{\pi a_1{}^3n^4(l+m^*)![(n+l)!]^3}\right\}^{1/2}\xi^l\epsilon^{-\xi}L_{n+l}^{2l+1}(2\xi)P_l{}^{m^*}(\mu)\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}m^*\phi \qquad (5)$$

The system (5) is orthogonal over all space, and is unitary when[17] $m_l\neq 0$.

[16] For a statement of conventions adopted with regard to the axial quantum number see L. Brillouin, Jour. de Physique et Rad., **7**, 74 (1927).

When a strong electric field is allowed to perturb the atom the type of quantization changes, and to separate the variables in the amplitude equation parabolic coordinates λ_1, λ_2, and ϕ must be used[7,8]. These are defined by their relations to the Cartesian coordinates: $x=+(\lambda_1\lambda_2)^{1/2}\cos\phi$, $y=+(\lambda_1\lambda_2)^{1/2}\sin\phi$, and $z=1/2(\lambda_1-\lambda_2)$. We consider here the orthogonal set of eigenfunctions satisfying Schroedinger's boundary conditions for the case of a vanishing field (the "null approximation"), and denote an eigenfunction by Φ. The system of functions Φ, unitary when $m_l\neq 0$, is[17]:

$$\Phi=\left\{\frac{Z^{2m^*+3}p!(n-m^*-p-1)!}{\pi a_1{}^{2m^*+3}n^{2m^*+4}[(m^*+p)!(n-p-1)!]^3}\right\}^{1/2}(\lambda_1\lambda_2)^{m^*/2}$$

$$\epsilon^{-(\lambda_1+\lambda_2)Z/2na_1}L^{m^*}_{m^*+p}(Z\lambda_1/na_1)L^{m^*}_{n-p-1}(Z\lambda_2/na_1)\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}m^*\phi \quad (6)$$

The parameters l, p, etc., in (5) and (6) are the quantum numbers defined in Section 2.

In our case, the case of an atom perturbed by a strong electric field, the functions Φ must be used. In Heisenberg and Jordan's problem the functions Ψ are used. We shall show now that for fixed n and m_l there exists a linear dependence between the two types of eigenfunctions, namely, that the expansion

$$\Phi(n,m_l,p)=\sum_{l=m}^{n-1}{}^{*}C(n,m_l,p,l)\Psi(n,m_l,l) \quad (7)$$

exists. We shall write this for brevity $\Phi_p=\Sigma_l C_{pl}\Psi_l$.

The functions Φ above were found in the null approximation, i.e., the problem was set up as if there were a field, but in the final result the field was neglected. This means that the functions Φ can also be found by treating the problem of an unperturbed Newtonian hydrogenic atom, without spin, and using parabolic coordinates. Now, the eigenvalues of energy of such an atom depend only on the principal quantum number, and it therefore follows that if the value of n is fixed, then any one Φ_p is a uniquely determined linear function of the set of functions Ψ_l, and *vice versa*. Consideration of orthogonality leads to the conclusion that only a single value of m_l can appear in the linear relationship, and thus the existence of Eq. (7) is proved. In the remainder of this paper we shall make frequent use of the coefficients C_{pl}, but to evaluate them here would mean an untimely digression from our main object. Therefore we state here, without a proof, that the value of C_{pl} is given by Eq. (23) below, and postpone the proof until Section 9.

6. *Average values of* $f(r)$. In calculating the relativity and the spin corrections for the case of a strong electric field we shall need to know the average values of certain functions of r, the "radius vector" of the electron, taken with respect to the unperturbed system. Thus, in accordance with

[17] When $m_l=0$ the factor $2^{-1/2}$ must be introduced to normalize the system to unity.

the Schroedinger's field theory, we shall need to calculate integrals of the type:

$$\overline{f(r)}_{par}=\int\int\int \Phi_p{}^2 f(r)dv, \tag{8}$$

where the subscript "*par*" is used to indicate the "parabolic" type of quantization, appropriate to the case of a strong electric field. If, as in the case of Heisenberg and Jordan's problem, the unperturbed system consists of a Newtonian hydrogenic atom, without spin and without an external field, the needed averages are of the form:

$$\overline{f(r)}_{pol}=\int\int\int \Psi_l{}^2 f(r)dv,$$

where the subscript "*pol*" indicates the "polar" type of quantization, appropriate to the case of a weak external field. Eliminating Φ_p from (8) by (7), we now find that, due to the orthogonality of the tesseral harmonics involved in Ψ_l, the following relation exists:

$$\overline{f(r)}_{par}=\sum_l C_{pl}{}^2\overline{f(r)}_{pol}. \tag{9}$$

This relation is useful, as, in general, the functions Ψ are somewhat easier to handle that the functions Φ. In our case this relation is particularly useful, since the expressions we shall need for the right hand side of (9) were explicitly given by Heisenberg and Jordan.[4] Their results are, in our notation:

$$(\overline{r^{-1}})_{pol}=Z/a_1n^2,\quad (\overline{r^{-2}})_{pol}=Z^2/a_1{}^2n^3(l+\tfrac{1}{2}),$$
$$(\overline{r^{-3}})_{pol}=Z^3/a_1{}^3n^3l(l+\tfrac{1}{2})(l+1).$$

Application of (9) gives:

$$\left(\overline{\frac{1}{r}}\right)_{par}=\frac{Z}{a_1n^2},\qquad \left(\overline{\frac{1}{r^2}}\right)_{par}=\frac{Z^2}{a_1{}^2n^3}\sum_l C_{pl}{}^2/(l+\tfrac{1}{2}),$$

$$\left(\overline{\frac{1}{r^3}}\right)_{par}=\frac{Z^3}{a_1{}^3n^3}\sum_l\frac{C_{pl}{}^2}{l(l+\tfrac{1}{2})(l+1)}. \tag{10}$$

7. *The relativity and the spin corrections in a strong electric field.* The perturbing potential equivalent to the relativity correction is in this case given, if terms of the order of F/c^2 are neglected, by[18]

$$V_{rel}=-1/2mc^2\cdot(W_0+Ze^2/r)^2,$$

where W_0 is the energy of the unperturbed system, and is given by (2).

[18] J. H. Van Vleck, *Quantum Principles and Line Spectra*, Bul. Nat. Res. Council, No. 54 (1926), p. 66.

The correction to be added to the energy of the unperturbed system in order to account for the effects of relativity is the average of V_{rel} over the unperturbed system, i.e.,

$$W_r^{(0)} = -1/2mc^2 \cdot \left\{ W_0^2 + 2e^2ZW_0(\overline{r^{-1}})_{par} + e^4Z^2(\overline{r^{-2}})_{par} \right\}.$$

For any experimentally attainable field strength the terms depending on F in W_0 are negligible in comparison to $-e^2Z^2/2a_1n^2$, so that we neglect these. Substitution and reduction then gives Eq. (18) below.

The spin correction for the energy of an hydrogenic atom in a strong electric field is[4,19]: $e^2h^2Zm_lm_s(\overline{r^{-3}})/8\pi^2m^2c^2$. In the case of a strong electric field the average of r^{-3} is the "parabolic" average. Substitution and reduction gives Eq. (19*a*) below, where the condition $m_l \neq 0$ is introduced, since, when $m_l = 0$, the summation reduces to one term, $l = 0$, and this term is indeterminate.

We now observe that, if $m_l \neq 0$, the spin correction in a strong electric field is formally equal to a summation, with coefficients C^2_{pl}, of spin corrections in a strong magnetic field. Extrapolating this observation to the case $m_l = 0$, we obtain Eq. (19*b*). Here we multiply by C^2_{pl} (this equals $1/n$ when $l = m_l = 0$) the expression $16\Delta W_H Z^4/n^3$ which is the spin correction appropriate to a level $l = m_l = 0$ for either a weak or a strong magnetic field.[4]

We might add at this point that we have applied numerically the relativity and the spin corrections developed here to the various experimental studies of H_γ referred to by Wentzel[6] and by Waller,[8] account being taken of the relative intensities of components. The shifts, in strong fields, of the mid-components (i.e., of components not affected by the linear Stark effect) have been heretofore interpreted as due to the quadratic Stark effect alone, and the agreement with experiment was found by various writers to be not quite perfect, though much better than on the Bohr theory. It was thought at the beginning of the present investigation that these discrepancies might be due to the omission of the relativity and spin corrections, but calculation showed the corrections to be, on the whole, negligible. For example, the shift, *as measured on the photographic plate*, of the center of gravity of the mid-components of H_γ for $F = 147$ kv per cm, relative to the center of gravity of the fine structure of H_γ in the absence of a field, was considered. It was found that the shift toward the red should be by about .01 Å greater than that given by the quadratic term of (2) alone. This is in the desired direction, but not of sufficient magnitude to bring agreement with the observed value.

[19] The reference given[4] is to the magnetic case. In the case of a strong electric field we consider the vector $\mathbf{I}$ as precessing rapidly about the direction of the field, and the coupling between $\mathbf{s}$ and $\mathbf{I}$ as broken down. The vector $\mathbf{s}$, which is affected only by magnetic forces, is then thought to precess about the average of the magnetic moment which is due to the orbital angular momentum of the atom. The average of $\mathbf{I}$ is in the direction of the external field, and therefore $\mathbf{s}$ precesses about the field. Thus m_lm_s appears instead of $\mathbf{s} \cdot \mathbf{I}$ in the expression for the energy, making the value of the latter formally identical with that for the magnetic case.

The separation of the components of the spin doublets was found to be nearly $2\Delta\nu_H/3$.

8. *Summary.* We tabulate here the formulas, calculated on the basis of the new quantum mechanics, relative to the energy levels of an hydrogenic atom perturbed by a weak or by a strong external electric field, which is homogeneous and constant. References to the sources of the previously published formulas are found in the Introduction.

When an hydrogenic atom is perturbed by a *weak* electric field its energy levels, to terms in F^2, are:

$$W(n,l,j,m)=W_0+W_{r,s}^{(0)}+W^{(1)}+W^{(2)}, \tag{11}$$

where:

$$W_0=-e^2Z^2/2a_1n^2, \tag{12}$$

$$W_{r,s}^{(0)}=\frac{16\Delta W_HZ^4}{n^3}\left(\frac{3}{4n}-\frac{1}{j+\frac{1}{2}}\right), \tag{13}$$

$$W^{(1)}=\frac{3a_1eFn(l-j)}{2Zj(j+1)}\left\{[n^2-(j+\tfrac{1}{2})^2]m^2\right\}^{1/2}, \tag{14}$$

$$W^{(2)}\ \ (when\quad j<n-\tfrac{1}{2})=\frac{9a_1{}^2e^2F^2n^5(j+\frac{1}{2})}{512\Delta W_HZ^6} \tag{15a}$$

$$\times\left\{\frac{(j^2-m^2)(j-\frac{1}{2})}{j^2}[2n^2-(j-\tfrac{1}{2})^2-(j+\tfrac{1}{2})^2]\right.$$

$$\left.-\frac{[(j+1)^2-m^2](j+\frac{3}{2})}{(j+1)^2}[2n^2-(j+\tfrac{1}{2})^2-(j+\tfrac{3}{2})^2]\right\},$$

$$W^{(2)}\ \ (when\quad j=n-\tfrac{1}{2})=\frac{9a_1{}^2e^2F^2n^6(n-1)[(n-\frac{1}{2})^2-m^2]}{128\Delta W_HZ^6(n-\frac{1}{2})}. \tag{15b}$$

When an hydrogenic atom is perturbed by a *strong* electric field its energy levels, to terms in F^2, are:

$$W(n,m_s,m_l,n_F,p)=W_0+W_r^{(0)}+W_s^{(0)}+W^{(1)}+W^{(2)}, \tag{16}$$

where:

$$W_0=-e^2Z^2/2a_1n^2, \tag{17}$$

$$W_r^{(0)}=\frac{16\Delta W_HZ^4}{n^3}\left(\frac{3}{4n}-\sum_{l=m}^{n-1}{}^*\frac{C_{pl}{}^2}{l+\frac{1}{2}}\right), \tag{18}$$

$$W_s^{(0)}(when\quad m_l\neq 0)=\frac{16\Delta W_HZ^4m_lm_s}{n^3}\sum_{l=m}^{n-1}{}^*\frac{C_{pl}{}^2}{l(l+\frac{1}{2})(l+1)}, \tag{19a}$$

$$W_s^{(0)}(when\quad m_l=0)=16\Delta W_HZ^4/n^4, \tag{19b}$$

$$W^{(1)}=-3a_1eFnn_F/2Z, \tag{20}$$

$$W^{(2)} = -\frac{\alpha^2 a_1^2 e^2 F^2}{512\Delta W_H Z^4} n^4(17n^2 - 3n_F^2 - 9m_l^2 + 19). \qquad (21)$$

The various physical constants and quantum numbers occurring here are described in Section 2. The coefficients C_{pl} are defined by Eq. (23)below. The relation between the levels for the two kinds of the external field is as follows: when the external field, originally weak, is gradually increased until it is strong, an energy level (11) passes over into a level (16), in which the quantum numbers are correlated with those in (11) according to the scheme[9]:

$$\textit{when } m>0: \; m_s = j-l, \; m_l = \quad m-j+l, \; n_F = n+|m|-l-j-1,$$
$$p = \tfrac{1}{2}(j-|m|+l-|m_l|), \qquad (22a)$$

$$\textit{when } m<0: \; m_s = l-j, \; m_l = -|m|+j-l, \; n_F = n+|m|-l-j-1,$$
$$p = \tfrac{1}{2}(j-|m|+l-|m_l|). \qquad (22b)$$

The coefficients C_{pl} are given by the relation[20]:

$$\begin{aligned} C_{pl} &= C(n, m_l, p, l) \\ &= l!\{[2l+1](n-l-1)!p!(n-m^*-p-1)!(m^*+p)!(n-p-1)!(l-m^*)!(l+m^*)!\}^{1/2} \\ &\quad \times\{(n+l)!\}^{-1/2} \sum_i \{(-1)^{i+1}(m^*+i)!(p-i)!i!(l-i)! \\ &\qquad (n-p-l-1+i)!(l-m^*-i)!\}^{-1}. \end{aligned} \qquad (23)$$

The meaning of these coefficients is discussed in Section 5, the validity of Eq. (23) is proved in Section 9, and certain numerical values of C_{pl} are given in Section 10. It must be noted that when C_{pl} occurs in the summations in the formulas relative to strong fields, the parameter l is not the true azimuthal quantum number, which loses its meaning in the case of a strong electric field, but a running variable in a formal summation over the different azimuthal levels appropriate to a weak field.

9. *Evaluation of C_{pl}.* In Section 5 we proved the existence of the expansion (7), and quoted, without proof, Eq. (23) for the evaluation of the coefficients C_{pl}. In this Section we shall prove that Eq. (23) is valid. The usual method for finding Fourier coefficients by integration leads in our case to integrals and summations of some complexity, and therefore a different method is resorted to, which we shall outline briefly.

We first eliminate the variables λ_1, and λ_2 from (6) by means of the variables ξ and μ, defined in Section 5. Then we cancel certain factors common to Ψ_l and Φ_p, and, using D_μ for $d/d\mu$, obtain the expressions:

$$\Psi_l' = \left\{\frac{[2l+1](l-m^*)!(n-l-1)!}{(l!)^2(l+m^*)![(n+l)!]^3}\right\}^{1/2} \xi^l L_{n+l}^{2l+1}(2\xi) D_\mu{}^{m^*+l}(\mu^2-1)^l,$$

$$\Phi_p' = \left\{\frac{p!(n-m^*-p-1)!}{[(m^*+p)!(n-p-1)!]^3}\right\}^{1/2} \xi^{m^*} L_{m^*+p}^{m^*}[\xi(1+\mu)] L_{n-p-1}^{m^*}[\xi(1-\mu)]$$

[20] The limits of summation are awkward to indicate explicitly. They are such that within them every factorial in every term of the sum exists. ($k!$ exists if $k=0, 1, 2, \cdots$.)

The coefficients in the expansion $\Phi_p' = \Sigma_l C_{pl} \Psi_l'$ are the same as those in (7), and, furthermore, the restriction $m_l \neq 0$ is no longer necessary. We now expand Ψ' and Φ' as polynomials in the two variables ξ and $\alpha = \frac{1}{2}(1+\mu)$, and find that, if d and t are integers, then[20]

$$\Psi_l' = \sum_d \sum_t \sum_q \frac{(-1)^{d+t+m^*+1} 2^{d-m^*} l! \{[2l+1](l-m^*)!(n-l-1)!(m^*+l)!(n+l)!\}^{1/2}}{(l+d+1)!(n-d-1)!(d-l)!(l-q)!(q+m^*)!q!(l-m^*-t)!(t-q)!} \xi^d \alpha^t,$$

$$\Phi_p' = \sum_d \sum_t \sum_i \frac{(-1)^{d+t+m^*+i} 2^{d-m^*} \{p!(n-m^*-p-1)!(m^*+p)!(n-p-1)!\}^{1/2}}{(m^*+i)!(p-i)!i!(d-i)!(n-p+i-d-1)!(d-m^*-t)!(t-i)!} \xi^d \alpha^t.$$

The presence of any particular term depends on the existence of every factorial in its coefficient, and on that only. Thus, suitable numbers n, m^*, p, d, and t, being fixed, there can be found one corresponding term in Φ_p', and, in general, several corresponding terms among the terms in the set $\Psi'_{l=m^*}$, $\Psi'_{l=m^*+1}$, $\cdots$, and $\Psi'_{l=n-1}$, as the coefficients of the latter depend on the parameter l. However, if, in particular, we look for terms such that $t = d - m^*$, we find that the factorials $(d-l)!$ and $(l-m^*-t)!$ entering in Ψ_l' become $(d-l)!$ and $(l-d)!$, respectively, so that for their simultaneous existence it is necessary and sufficient that l have the particular value d. In other words, among all the terms of the set of functions Ψ_l' there is one, and only one term which can be matched with the term involving $\xi^d \alpha^{d-m^*}$ in Φ_p', and, furthermore, this term comes from $\Psi'_{l=d}$.

TABLE I. *Certain numerical values of the coefficients* C_{pl}.

	$n=2, m^*=0$		$n=3, m^*=0$			$n=3, m^*=1$	
p	$l=0$	1	$l=0$	1	2	$l=1$	2
0	$-2^{-1/2}$	$-2^{-1/2}$	$-3^{-1/2}$	$-2^{-1/2}$	$-6^{-1/2}$	$-2^{-1/2}$	$-2^{-1/2}$
1	$-2^{-1/2}$	$2^{-1/2}$	$-3^{-1/2}$	0	$(2/3)^{1/2}$	$-2^{-1/2}$	$2^{-1/2}$
2			$-3^{-1/2}$	$2^{-1/2}$	$-6^{-1/2}$		

	$n=4, m^*=0$				$n=4, m^*=1$			$n=4, m^*=2$	
p	$l=0$	1	2	3	$l=1$	2	3	$l=2$	3
0	$-\frac{1}{2}$	$-(9/20)^{1/2}$	$-\frac{1}{2}$	$-20^{-1/2}$	$-(3/10)^{1/2}$	$-2^{-1/2}$	$-5^{-1/2}$	$-2^{-1/2}$	$-2^{-1/2}$
1	$-\frac{1}{2}$	$-20^{-1/2}$	$\frac{1}{2}$	$(9/20)^{1/2}$	$-(2/5)^{1/2}$	0	$(3/5)^{1/2}$	$-2^{-1/2}$	$2^{-1/2}$
2	$-\frac{1}{2}$	$20^{-1/2}$	$\frac{1}{2}$	$-(9/20)^{1/2}$	$-(3/10)^{1/2}$	$2^{-1/2}$	$-5^{-1/2}$		
3	$-\frac{1}{2}$	$(9/20)^{1/2}$	$-\frac{1}{2}$	$20^{-1/2}$					

	$n=5, m^*=0$					$n=5, m^*=1$			
p	$l=0$	1	2	3	4	$l=1$	2	3	4
0	$-5^{-1/2}$	$-(2/5)^{1/2}$	$-(2/7)^{1/2}$	$-10^{-1/2}$	$-70^{-1/2}$	$-5^{-1/2}$	$-(3/7)^{1/2}$	$-(3/10)^{1/2}$	$-14^{-1/2}$
1	$-5^{-1/2}$	$-10^{-1/2}$	$14^{-1/2}$	$(2/5)^{1/2}$	$(8/35)^{1/2}$	$-(3/10)^{1/2}$	$-14^{-1/2}$	$5^{-1/2}$	$(3/7)^{1/2}$
2	$-5^{-1/2}$	0	$(2/7)^{1/2}$	0	$-(18/35)^{1/2}$	$-(3/10)^{1/2}$	$14^{-1/2}$	$5^{-1/2}$	$-(3/7)^{1/2}$
3	$-5^{-1/2}$	$10^{-1/2}$	$14^{-1/2}$	$-(2/5)^{1/2}$	$(8/35)^{1/2}$	$-5^{-1/2}$	$(3/7)^{1/2}$	$-(3/10)^{1/2}$	$14^{-1/2}$
4	$-5^{-1/2}$	$(2/5)^{1/2}$	$-(2/7)^{1/2}$	$10^{-1/2}$	$-70^{-1/2}$				

	$n=5, m^*=2$			$n=5, m^*=3$	
p	$l=2$	3	4	$l=3$	4
0	$-(2/7)^{1/2}$	$-2^{-1/2}$	$-(3/14)^{1/2}$	$-2^{-1/2}$	$-2^{-1/2}$
1	$-(3/7)^{1/2}$	0	$(4/7)^{1/2}$	$-2^{-1/2}$	$2^{-1/2}$
2	$-(2/7)^{1/2}$	$2^{-1/2}$	$-(3/14)^{1/2}$		

This property of the functions, together with the existence of the expansion (7), enables us to write:

$$C(n,m_1,p,l)=C_{pl}=\frac{coefficient\ of\ \xi^l\alpha^{l-m^*}\ in\ \Phi'(n,m_1,p)}{coefficient\ of\ \xi^l\alpha^{l-m^*}\ in\ \Psi'(n,m_1,l)}.$$

Reduction of this expression leads to (23).

10. *A table of numerical values of* C_{pl}. Numerical values of the coefficients C_{pl} are calculated by substituting the proper values of the parameters into (23), and summing with respect to the running variable i. The values so obtained can be checked by the relations $\Sigma_l C_{pl}^2=1$, $\Sigma_l C_{pl}C_{p'l}=0$, etc., which follow from the orthogonality and normalization of Ψ and Φ. As (23) implies somewhat tedious arithmetic, we give the accompanying brief Table I of values of C_{pl} for the first few values of the quantum number n. We omit the values for the cases in which $m^*=n-1$, as then $p=0$, $l=n-1$, and $C_{pl}=-1$.

II. Relative Intensities of the Stark Components

11. *The case of a weak field.* The application of the matrix mechanics to the evaluation of the energy states of an hydrogenic atom in a weak external electric field, carried out in Section 3, can be easily extended to the evaluation of the relative intensities of the corresponding Stark components. To this end we evaluate the matrix $\boldsymbol{q}_1$, the coordinate matrix in the presence of a weak electric field, by the relation $\boldsymbol{q}_1=\boldsymbol{S}\boldsymbol{q}\tilde{\boldsymbol{S}}^*$. Here $\boldsymbol{S}$ is the transformation matrix given on page 5, and $\boldsymbol{q}$ is the coordinate matrix in the absence of a field. The method of calculating the elements of the latter, to which we refer as the q's, was discussed in Section 3. The relative intensities of transitions in a weak electric field are proportional to the squares of the corresponding transition amplitudes, and these are the proper elements of $\boldsymbol{q}_1$.

When numerical values of the relative intensities are required, we can find the q's for the more important lines by using published tables[21] of relative intensities of the unresolved components of atomic hydrogen, instead of by performing the integration (4). We carry out the resolution by means of the sum-rule[14] and of the appropriate Kronig's factors.[15] Then the absolute magnitudes of the relative values of the q's can be found by taking the square roots of the resolved intensities, but an additional argument is required for the determination of their relative signs, i.e., the "phase" factors. To supply this argument we recall that transitions in the quantum number n correspond, on the basis of the Bohr theory, to transitions associated with the "main revolution frequency" ω_n of the electron. Now, examination of the classical Fourier expansion shows that the relative signs of the different combination overtones involving a given harmonic $\tau\omega_n$ of ω_n are independent of the order τ of this harmonic. Thus the *relative* signs of the amplitudes do not depend on the transition in n, but are determined by the transitions in the other

[21] Y. Sugiura, Jour. de Physique et de Rad., **8**, 113 (1927); F. G. Slack, Phys. Rev., **31**, 527 (1928); A. Kupper, Ann. d. Physik, **86**, 511 (1928).

quantum numbers. These signs are easily determined by integration of (4) when $n \to n$. We tabulate them below.

$m \to m$	$m \to m+1$	$m \to m-1$
$l \to l+1$ (+)	$l \to l+1$ (−)	$l \to l+1$ (+)
$l \to l-1$ (+)	$l \to l-1$ (+)	$l \to l-1$ (−)

12. *The question of metastability of the level* $2s$. This level is generally considered metastable, as the "polar" type of quantization is usually assumed and thus a transition down from $2s$ violates the selection rules. Now, the Dirac "quantum theory of the electron" shows that, in the absence of an external field, the levels $2s$ and $2p_1$ form a degenerate pair. Thus any linear combination of their wave functions can be taken equally well as the proper solution of the Schroedinger's wave equation, and in this infinity of possibilities there is but one case, i.e., the case in which the coefficient of the $2p_1$ part is zero, which leaves $2s$ metastable. If the atom is acted on by weak external electric field F the degeneracy is removed, as shown by Eq. (14) and the two originally coincident levels are transformed into a pair of levels whose separation is proportional to F. Applying the method for finding the amplitudes of transitions in a weak field outlined in the preceding Section, and denoting amplitudes in the field by q_1, and in polar quantization by q, we find that

$$q_1(2p_1 \to 1s) = q_1(2s \to 1s) = 2^{-1/2} q(2p_1 \to 1s).$$

Squaring these expressions shows that in the presence of a weak electric field the intensities of the transitions from $2p_1$, and from $2s$ down to $1s$ are equal. Thus in a weak electric field the level $2s$ in atomic hydrogen is not metastable. Now, the terms *weak* electric field implies only an upper limit to the field strength. Any electric field, then, however small, is sufficient to cause the breakdown of the metastability of the level $2s$, and, as in experiments with atomic hydrogen small ionic fields are unavoidably present, we conclude that it should be impossible to detect experimentally that $2s$ is a metastable state in unperturbed atoms. This is in agreement with the recent experimental results of Ornstein, Zernike, and Snoek,[22] and we consider this an important experimental support of the validity of the present theory.

13. *The case of a strong field.* Schroedinger[7] and Epstein[6] have investigated, neglecting the effect of spin, the relative intensities of the Stark components of hydrogen in a strong field, and calculated their numerical values for the prominent lines of the Balmer series. We shall show here how the calculation of the relative intensities of the lines in a strong field can be reduced to the calculation of the relative intensities of lines in the absence of a field. To this end we recall that in the case of a strong electric field the amplitudes of transitions can be evaluated from a relation which is similar to (4), except that the functions Φ must be used instead of the

[22] L. S. Ornstein, F. Zernike and J. L. Snoek jun., Zeits f. Physik, **47**, 627 (1928).

functions Ψ. Elimination of Φ from this relation by means of (7) leads to the formula:

$$q_i(n,m_l,p\ ;n',m_l',p') = \sum_l \sum_{l'} C(n,m_l,p,l)C(n',m_l',p',l')i(n,m_l,l\ ;n',m_l',l'), \quad (24)$$

where i equals x, y, or z. The elements of the coordinate matrices in the summation can be found numerically from the existing tables by the methods discussed in Section 11, care being taken to use the proper "phase" factors (cf. p. 14). The intensities of the components of a spin doublet are equal in strong electric fields, as the spin is quantized separately, and as positive and negative values of m_s have equal a priori probabilities.

It is a pleasure for the writer to express here his gratitude to Professor J. H. Van Vleck, under whose guidance this work was carried out at the University of Minnesota. Thanks of the writer are also due to Dr. E. L.Hill for numerous discussions.

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THE FURNACE SPECTRUM OF BERYLLIUM

By R. F. Paton and G. M. Rassweiler

Abstract

A *high-temperature vacuum furnace* using tungsten for container, and heating elements as well, has been designed to study the furnace spectra of high melting point substances. The furnace spectrum of beryllium in both absorption and emission has been observed from λ2150A–7000A and over a range of temperature up to 2500°K. The prediction that the beryllium line 2348.62A is the first line of the principal series of singlets for the neutral atom has been successfully confirmed and the diffuse and the sharp series of singlets of this element discovered and tabulated.

Introduction

THE work on the spectrum of beryllium before 1921 is conveniently summarized by Kayser and Konen[1] who list only twelve lines for this element. Since that time, new lines have been reported by Glaser,[2] Millikan and Bowen,[3] and others. In this laboratory, an extensive study has been made of the beryllium spectrum by Paton, Sanders, and Albers. They used the vacuum spark source in the wave-length range below 5300A and the spark and arc in air for the range 5000A to 9000A.

The absorption and emission spectra of the element have never been studied with a furnace, though an absorption spectrum by the underwater-spark method has been photographed by Allin and Ireton.[4] They observed the absorption of five well-known multiplets, all unresolved; of the singlet 2348A, unresolved from the triplet 2350A; and of the line 2175A which they claim was first observed in their laboratory by McDonald, Sutton and McLay, but which was actually discovered by Rowland and Tatnall in 1895.[5] Only one of these lines (2348A) is of unknown series identification. Thus, while these underwater-spark data are of considerable interest they do not aid in further work on series relationships.

The only important works on series in the beryllium spectrum are by Back,[6] and Millikan and Bowen. The former studied the Zeeman effect of several lines and made predictions regarding their series relationships although he was unable to set up such series due to the scarcity of observed beryllium lines. Millikan and Bowen, using Back's data together with their own observations in the extreme ultra-violet, succeeded in establishing a set of triplet series of Be I and a set of doublet series of Be II and in calculating the first few term values in each of these series. The singlet series

[1] Kayser and Konen, Handbuch der Spectroscopie, Vol. VII (1924).
[2] Glaser, Ann. d. Physik, **68**, 73 (1922).
[3] Millikan and Bowen, Phys. Rev., **28**, 256 (1926).
[4] Allin and Ireton, Roy. Soc. Can. Trans., **21**, 127 (1927).
[5] Rowland and Tatnall, Astrophys. J., **1**, 14 (1895).
[6] Back, Ann. d. Physik, **70**, 333 (1923).

of Be I have never been published and in fact only two lines, 2348.62A and 4572.69A, have ever been assigned to the singlet system (by Back from their normal Zeeman effect).

It was the purpose of this investigation to design and construct a furnace suitable for the study of the spectrum of metallic vapors, to use this in the study of the absorption and emission spectrum of beryllium, and to see if the data obtained would shed any light on the series identifications of the singlet lines of the neutral atom.

Apparatus and Method

In designing a furnace for this investigation, the need for convenient control of furnace temperatures led to the choice of the electric resistance type. In order to be reasonably sure of securing a sufficient quantity of beryllium vapor, the maximum temperature desired in the furnace was about 2500°C. Both tungsten and carbon will stand such temperatures, and carbon furnaces have been successfully used by King and others. However, a preliminary experiment indicated that beryllium would react vigorously with carbon at high temperatures so tungsten was chosen for the electric resistance heating elements, the furnace being placed in a vacuum chamber to protect the tungsten and beryllium from oxidation.

A furnace of this type requires a high current at a low voltage for the resistance is small and the radiation losses large. The heating elements could not be packed in refractory material, and a satisfactory vacuum maintained at high temperatures. A 30 k.v.a., 25 volt, transformer was available and it remained to design a tungsten container which could be heated to the desired temperatures with the current available. Data on resistivity and radiation losses of tungsten have been published[7] for temperatures up to its melting point. Assuming radiation losses would occur from the outside walls and ends of the container, the surroundings remaining at room temperature, and that heat losses by conduction would be negligible, the power loss for any temperature could be computed. Then knowing the resistance of the tungsten at that temperature, it was possible to find the necessary current and potential drop in the heating elements. Later, tests on the furnace showed the actual temperature for any given current to be about 20 percent lower than the calculated value.

The only part of the furnace which is heated is the tungsten box. This is made up of four strips, 1.6 cm$\times$20 cm$\times$0.07 cm (kindly donated by the Fansteel Products Corporation), each strip forming one side of the box. The ends of the box are open. In order to hold the strips and make electrical contact with them, the ends of each strip are bent outwards at right angles. This makes the box, or tube, formed by the strips 14 cm long and 1.8 cm square in cross section. It is supported in a horizontal position and the beryllium to be vaporized is placed on the bottom strip in a small tungsten boat.

[7] Forsythe and Worthing, Astrophys. J., **61**, 147 (1925).

Fig. 1 shows the arrangement for supporting the tungsten although the strips themselves are not in place. These pass through the small square opening, and are held in place by brass plates screwed to the water-cooled brass blocks. The strips are electrically in series, the blocks being insulated from each other with glass and mica. Surrounding the main portion of the tungsten box is a water-cooled cylindrical radiation shield. The hot tungsten is thus almost completely surrounded by water-cooled brass parts protecting the rubber tubes from direct radiation. The block supports and radiation shield are all mounted on a half-inch brass plate which has a water-cooling chamber on its lower side. A heavy brass box which fits down over the apparatus shown on Fig. 1, constitutes the vacuum chamber. On each side of the box is an observation window of quartz mounted at the end of a brass tube which opens into the furnace directly in front of the end of the tungsten box.

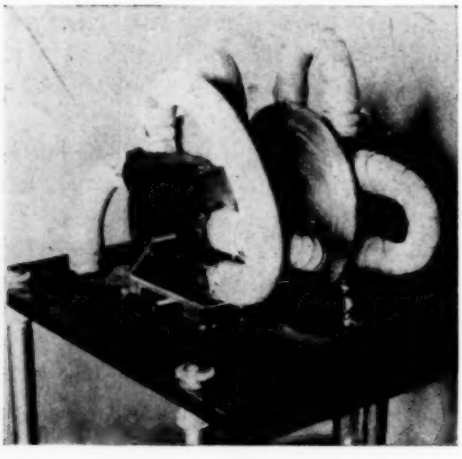

Fig. 1. Photograph of the tungsten furnace.

The temperature of the furnace is controlled by resistance units placed in the primary circuit of the transformer supplying the heating current. Temperatures are measured with an optical pyrometer of the disappearing filament type, the instrument being focussed on the end of the tungsten boat containing the beryllium inside the hot tungsten chamber. Temperature measurements are given to the nearest 50°C.

The operating characteristics of this furnace are very satisfactory. Pressures as low as 5×10^{-5} mm are obtained in the cold furnace and 2×10^{-4} mm at 1000°C. The maximum temperature actually used was 2250°C. High temperatures were never maintained for any longer time than was necessary to secure spectrograms (less than one minute), the brass vacuum chamber heating up rapidly in spite of the water-cooling system. The furnace currents were varied from about 140 amps. at 750°C to 550 amps. at 2250°C.

The continuous source used for the study of absorption effects was the under-water spark between copper electrodes. This was operated with

current from a 4 k.v.a., 60,000 volt, transformer and was intense enough to give exposures in from 8 to 16 seconds over the wave-length range studied (2150A to 7000A).

The spectrograph was a Hilger E1 with quartz optical system. The spectrograms were measured on a Gaertner comparator. In most cases, the measurements were only accurate enough to make identifications positive, but on some plates precision measurements were undertaken using the iron arc for comparison.

Results

Absorption. Observations were made in the wave-length range from 2150A to 7000A in an effort to locate absorption lines of beryllium. The vapor temperature was varied from 1200°C to 2200°C, and over most of this range, exposures were made at intervals of 100°C or less. The only beryllium absorption line which was observed was at 2348.62A. This absorption was first noted on an exposure made through the vapor at a temperature of 1550°C. The next exposure on this plate was at 1850°C and here the line showed as an emission line superimposed on the spectrum from the continuous source. A number of exposures were then made to determine the temperature at which the line would change from absorption to emission. It was found that absorption occurred between the temperatures 1400°C and 1800°C, but was never observed above 1800°C. Emission was observed as low as 1850°C although some exposures at this temperature showed neither absorption nor emission.

It seems remarkable that no other absorption lines should appear in the wide wave-length range studied. It is unlikely that this was due to the lack of sufficient vapor to give the effect, for the quantity of vapor necessary to produce absorption is very small indeed. This is shown by the absorption of a large number of iron lines on two of the spectrograms. The presence of iron vapor in the furnace at that time can only be explained by the fact that the tungsten boat had been ground on an emery-wheel immediately prior to heating the furnace for these pictures. The iron contamination from the emery-wheel must have been minute and the amount of iron vapor from this source very small compared to the beryllium vapor present. Also, the surprising ease with which absorption of 2348A was obtained at low temperatures indicates that only a small quantity of vapor is required to produce absorption. In fact, the absorption of 2348A still occurred after the furnace had been heated six times to temperatures above 1500°C without renewing the supply of beryllium. Whenever the supply of beryllium in the furnace was renewed, a large amount of vapor must have been produced on heating, as evidenced by the fogging of the observation windows.

The absorption at 2348A, and at this wave-length only, makes the series identification of this line quite positive. Its singlet character has already been proven by its normal Zeeman effect; its identity as a member of the principal series is shown by the ease with which it is absorbed, and its position as the first member of this series is demonstrated by the fact that

no other absorption occurred in the wave-length region studied. Thus the prediction of Back and others that 2348.62A is the first line of the principal series of the singlet system of neutral beryllium is confirmed.

Emission. The data on emission are grouped under two heads, namely, lines of previously known series (Table I) and lines whose series identification was made possible by this work (Table II). The former are listed in Table I,

TABLE I. *Emission of lines of known series.*

Wave-length A (air)	Series notation by Millikan	Intensity in furnace 1850°C	2250°C
	Triplet system of Be I.		
3321.35	$2p_1-3s$		
3321.09	$2p_2-3s$	2	8d
3321.02	$2p_3-3s$		
2350.78	$2p-4s$	0	5d
2494.63	$2p_1-3d$		
2494.48	$2p_2-3d$	1	6d
2494.44	$2p_3-3d$		
2175.04	$2p-4d$	—	4d
2650.77 to 2650.47	pp' group	—	2u
	Doublet system of Be II		
3131.07	$2s-2p_2$	—	4
3130.42	$2s-2p_1$	—	5

Note: u = diffuse; d = double but poorly resolved.

where a dash indicates that the line did not appear on any of the plates taken at that temperature. The only triplet lines of neutral beryllium lying in the wave-length region studied are the first two members of the diffuse series and the first two members of the sharp series. These four lines (the term "line" is applied to the multiplet) were observed and also the pp' group at 2650A. There are twelve lines in this region which are known to belong to the doublet system of singly ionized beryllium. Only one of these doublets, the first member of the principal series, was emitted by the vapor in the furnace and this pair faintly and only at the highest temperatures. The three lines in the visible region which appear the most intense in arc and spark sources are 4360.99A (Be II 3^2P-4^2D), 4673.25A (Be II 3^2D-4^2F) and 4572.69A (Be I 2^1P-3^1D). (These were all observed by Albers as intensity 10 in the vacuum spark.) It is interesting to note that neither of the first two lines, which belong to ionized beryllium, was observed on the spectrograms which have been measured. The line 4572A, however, appears with intensity estimated as 12. It is of course not a new observation that the furnace provides a means of sorting out lines emitted by the neutral atom from those emitted by the ionized atom but the fact is nicely illustrated by these data (Table I).

Table II was prepared by carefully analyzing a number of emission plates taken with the furnace at 2250°C in the wave-length region 2150A

to 7000A, computing the wave-lengths from the standard iron lines, then sorting out impurities by the usual methods. Examination of these data together with existing data on beryllium, including that of Sanders and Albers, was then undertaken.

TABLE II. *Singlet lines of Be I emitted at 2500°K*

Int.	λ(air)	ν(vacuum)	First observer	Series
—	8253.5	12112.8	Albers	2^1P-3^1S
12	4572.69	21862.86	Kirchhoff	2^1P-3^1D
5	4408.02	22679.58	Albers	2^1P-4^1S
8	3813.46	26215.49	Sanders	2^1P-4^1D
3	3736.30	26756.86	—	2^1P-5^1S
5	3515.57	28436.78	Sanders	2^1P-5^1D
3	3367.67	29685.62	—	2^1P-6^1D
1	3283.15	30449.80	Sanders	2^1P-7^1D
20	2348.62	42565.15	Rowland	2^1S-2^1P

Term Values

$2^1P-32615.01$	$2^1S-75180.15$	$3^1D-10757.14$	
	$3^1S-20502.21$	$4^1D-\ 6404.51$	
	$4^1S-\ 9940.42$	$5^1D-\ 4183.22$	
	$5^1S-\ 5863.14$	$6^1D-\ 2934.38$	
		$7^1D-\ 2170.20$	

This yielded a list of some fifteen lines that could be tentatively attributed to beryllium. Of these lines five, involving the strongest lines observed, suggested by their order and intensity a series of singlets. A more careful examination gave the typical diffuse series. Of the few remaining strong lines in the region, two, together with a line observed by Albers in the near infra-red, gave the sharp series. The limit of these series was computed by the method suggested by Johanson.[8] The term values are accurate to a few wave-numbers and give an ionization potential for beryllium of 9.277 equivalent volts.

A word should be said about the impurity lines on the emission spectrograms. Nearly all the iron lines which appeared on the two plates previously mentioned had already been assigned by King to Class I in the furnace. A few chromium, mercury, and barium lines also appeared. Two lines at 2397.11A and 2446.47A were attributed to tungsten though the amount of tungsten vapor even at 2200°C must have been minute. It is interesting also that the first five lines of the Balmer series of atomic hydrogen appeared at about 2200°C with estimated intensities of 10, 8, 4, 3, 2, respectively.

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UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
August 15, 1928.

[8] Johanson, Arkiv. f. Mat., Astron. och Fysik., **12**, No. 6 (1917).

MEASUREMENT OF THE LIFE OF THE METASTABLE MERCURY ATOM

By M. L. Pool

Abstract

Half value time for the 2^3P_0 state of Hg for various pressures of admixed N_2— A high speed rotating disk has been used to interrupt the total radiation from a water-cooled and magnetically controlled quartz mercury arc before optically exciting mercury vapor in a quartz resonance tube at room temperature. In the neighborhood of 10^{-4} sec. after the optical excitation a flash of visible radiation from another water-cooled and magnetically controlled mercury arc was passed through the resonance tube and the absorption spectrum photographed. The line 4047 ($2^3P_0 - 2^3S_1$) showed strong absorption when a few millimeters of nitrogen were introduced into the resonance tube. The lines 4077, 4358, 5461, 5770 and 5790 showed no measurable absorption under similar conditions. The rate of decay of the amount of 4047 absorbed with respect to the time-wait after excitation of the mercury vapor was taken as the rate of decay of the metastable 2^3P_0 state. The life or half-value time of the state was found to vary markedly with the pressure of admixed nitrogen. The maximum life 4.2×10^{-4} sec. occurred for 6.8 mm of nitrogen. No absorption of 4047 was observed upon the introduction of hydrogen, argon, neon, or helium into the resonance tube.

Introduction

In attempting to measure the life of the metastable states of the mercury atom two methods depending upon the means employed to produce the metastable atom have been used. The method of interrupted electrical

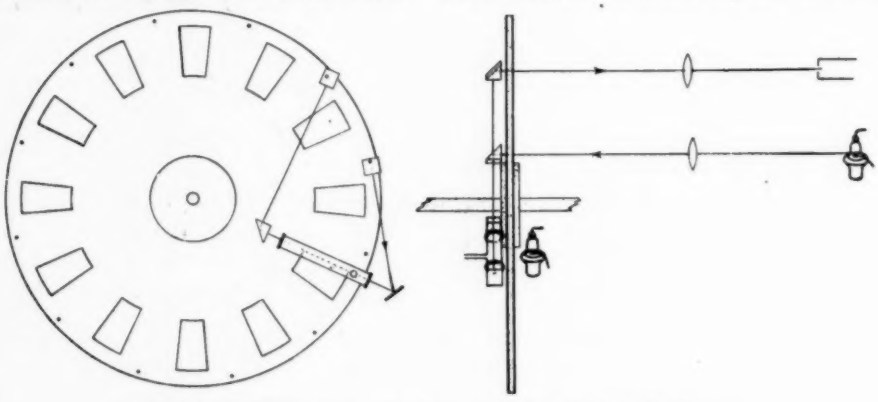

Fig. 1. Arrangement for interrupted optical excitation.

excitation has given lives of extremely long value (1/200 to 1/22 sec.).[1] Underlying these measurements, however, is the objection[2] that these metastable atoms may be formed from the recombination of electrons and positive ions which have been shown[3] to exist under some conditions as long as 1/10 sec. after the interruption of the exciting current.

[1] Marshall, Astrophys J., **60**, 244 (1924); Dorgelo, Physica, **5**, 429 (1925).
[2] Eckart, Phys. Rev., **26**, 453 (1925).
[3] Pool, Phys. Rev., **30**, 848 (1927).

The method of optical excitation with λ2537 avoids this objectional feature[4] by lifting the electron up to only the 2^3P_1 state. By means of the intensity of the fluorescence radiation (of thallium, say) in optically excited mercury vapor an estimate of the life of the 2^3P_0 state may be made.[5] The quenching of the resonance radiation of mercury in optically excited mercury vapor also gives information concerning the life of the metastable state.[6] The results of both these methods depend upon assumptions and measurements in which a large error may easily exist. In the two cases cited the life of the 2^3P_0 state was found to be about 3.5×10^{-4} sec. even under very different pressure and temperature conditions.

This paper is a report of the results of a direct interrupted optical excitation method for measuring the life of the metastable 2^3P_0 state in mercury.

Apparatus and Method

A quartz resonance tube containing mercury vapor at room temperature was excited optically by the total radiation from a 220 volt d.c. "Uviarc" quartz mercury arc. The arc was water-cooled and the discharge pressed against the side of the quartz tube by a weak magnetic field. The optical excitation of the resonance tube was interrupted by means of a disk as shown in Fig. 1. The disk was 20 cm in radius, made of bakelite, and could easily be run at 3000 r.p.m. Near the periphery of the disk holes one millimeter in diameter allowed flashes of light from a 110 volt d.c. arc, water-cooled and also magnetically controlled, to pass through the resonance tube shortly after it had been excited by the 220 volt arc. This interval or time-wait depended upon the position of the one millimeter holes, and the rotation speed of the disk. Photographs of the visible portion of the mercury spectrum were taken with and without the resonance tube excited and for various speeds of the rotating disk. Nitrogen was admitted to various pressures through $CaCl_2$ and P_2O_5. In the resonance tube there was a small drop of mercury.

Fig. 2. Photograph of 4358 and 4047 showing marked absorption of 4047 with decrease in time-wait after optical excitation.

Results

For a mixture of nitrogen of a few millimeters and mercury at room temperature in the resonance tube, the mercury line 4047 ($2^3P_0-2^3S_1$) always showed marked absorption within 10^{-4} sec. after the interruption of the optical excitation. The lines 4077, 4358, 5461,

[4] Meiszner and Graffunder, Ann. d. Physik, **84**, 1009 (1927).
[5] Loria, Nat. Acad. Sc., **11**, 673 (1925).
[6] Foote, Phys. Rev., **30**, 288 (1927).

5770 and 5790 showed at no time any measurable absorption even within 0.5×10^{-4} sec. after excitation of the resonance tube. An investigation of the amount of absorption of 4047 was made for various time-waits in order to obtain the rate of decay of the metastable 2^3P_0 state. It is assumed that the rate of decay of the amount of absorption of 4047 is also the rate of decay of the metastable state. A typical plate showing 4358 and 4047 is seen in Fig. 2. The increasing amount of absorption of 4047 with decreasing time intervals may be easily seen, while 4358 shows no absorption whatever. The first and last set of lines show the intensity of 4358 and 4047 when the mercury vapor in the resonance tube had not been excited. The percent absorption of 4047 at three different pressures of admixed nitrogen for various time-waits is shown in Table I. The amount of absorption was measured by a Moll microphotometer. A semi-logarithmic plot of the percent absorption against the

TABLE I. *Percent absorption of λ 4047 in Hg vapor for three different pressures of admixed N_2.*

4.8 mm N_2 Time-wait	Percent absorption	16 mm N_2 Time-wait	Percent absorption	38 mm N_2 Time-wait	Percent absorption
4.1×10^{-4} sec.	38.0	6.8×10^{-4} sec.	23.5	4.9×10^{-4} sec.	11.0
2.0 "	55.0	3.6 "	40.5	2.6 "	28.0
1.1 "	65.3	2.1 "	60.0	1.2 "	50.3
0.67 "	71.3	1.2 "	70.0	0.7 "	61.0
		0.71 "	75.3		

time-wait is shown in Fig. 3 for a number of pressures. It is seen that the rate of decay of the percent absorption is greatest for pressures in the

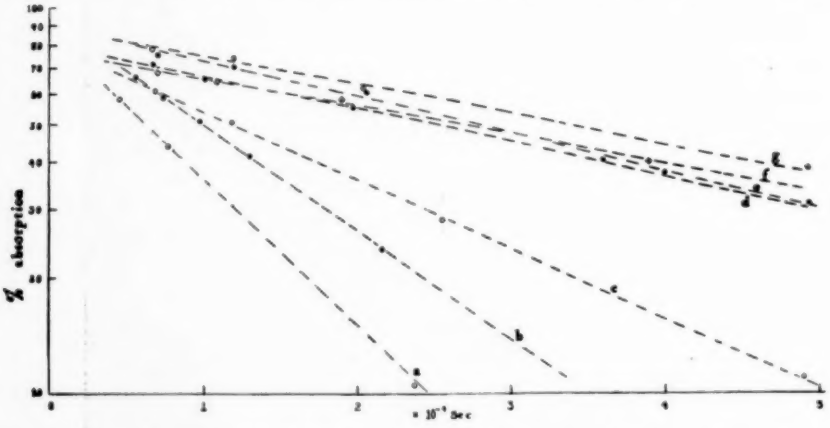

Fig. 3. Semi-logarithmic plot of percent absorption of 4047 in mercury vapor at room temperature with admixture of nitrogen against the time after optical excitation. Pressure of nitrogen for curves *a*, *b*, *c*, *d*, *e*, *f*, *g* is respectively 63, 2.5, 38, 4.8, 16, 6.8, 8.7 mm.

neighborhood of 2 and 50 mm of nitrogen. The rate is slowest for pressures of about 7 mm.

Table II shows the appearance of the visible resonance radiation during excitation of the resonance tube, the amount of admixed nitrogen, and the half value period, or life of the metastable 2^3P_0 state.

TABLE II. *Appearance of the resonance radiation and life of the metastable 2^3P_0 state for various pressures of N_2.*

Resonance radiation	Nitrogen pressure	Life of 2^3P_0 state
Weak	63.0 mm	0.76×10^{-4} sec.
Very weak	2.5 "	1.05 "
Strong	38.0 "	1.7 "
"	4.8 "	3.7 "
Very strong	16.0 "	3.2 "
" "	8.7 "	4.1 "
" "	6.8 "	4.2 "

In Fig. 4 the life of the 2^3P_0 state as well as the amount of absorption of 4047 at 6.8×10^{-4} sec. after optical excitation are plotted against the pressure of the admixed nitrogen. The longest life of the metastable state and also the greatest amount of absorption of 4047 is seen to occur when the nitrogen pressure is about 6.8 mm. From kinetic theory considerations Foote calculated for rather weak optical excitation a maximum concentration of 2^3P_0 states for 2.0 mm of nitrogen.[6] It is also seen that the life does not

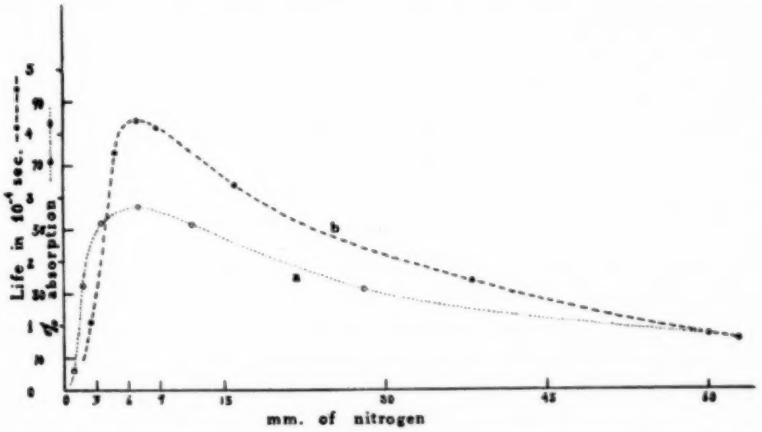

Fig. 4. Curve *a*, percent absorption of 4047 in mercury vapor at room temperature 0.68×10^{-4} sec. after optically excited plotted against pressure of admixed nitrogen. Curve *b*, life of the 2^3P_0 state in mercury at room temperature plotted against pressure of admixed nitrogen.

decrease inversely proportional to the pressure of admixed nitrogen.[5] The short life and also the small amount of absorption obtained for pressures less than about three millimeters of nitrogen may be due to a small number of 2^3P_0 atoms produced, their subsequent diffusion to the walls of the resonance tube, and the narrowness of the center absorbed from the incident 4047.[7] Asada, Ladenburg and Tietze[8] have recently reported an interrupted optically excited absorption and emission method which gave a life of 15×10^{-4} sec. with the admixture of one millimeter of nitrogen.

[7] Wood and Gaviola, Phil. Mag., **6**, 271 (1928).
[8] Asada, Ladenburg, Tietze, Phys. Zeits., **29**, 549 (1928).

The introduction of helium at pressures 33, 13.5 and 5.1 mm into the resonance tube containing mercury at room temperature gave no absorption for time-waits longer than 0.5×10^{-4} sec., even though at 5.1 mm the visible resonance radiation during the time of excitation was quite strong. Argon, neon, and hydrogen at various pressures also gave no absorption of 4047. Nitrogen at 7.3 mm with hydrogen at 0.14 to 0.3 mm gave no absorption. It was not possible to make absorption measurements during the time of optical excitation. Nitrogen that had been standing in P_2O_5 for many days gave little or no absorption while the introduction of water vapor or fresh nitrogen from a tank greatly increased the amount of 4047 absorbed.

The points of importance in this paper are that the metastable 2^3P_0 state in mercury has been shown by a direct experiment to actually exist for a long length of time, that the life of the state depends upon the pressure of admixed nitrogen, and that the maximum life was found to be 4.2×10^{-4} sec.

This experiment was carried out in the Ryerson Physical Laboratory of the University of Chicago. It is the author's pleasure to express his warm appreciation to Professor A. J. Dempster and Dean H. G. Gale for the excellent facilities provided.

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HEATS OF LINKAGE OF C-H AND N-H BONDS FROM VIBRATION SPECTRA

By Joseph W. Ellis

Abstract

The visible and near infra-red absorption data for several representative molecules are taken from a previous paper and fitted to the formula of an anharmonic vibrator, $\nu^n = \omega^0 n - bn^2$. The mechanical frequencies, $\omega^n = \omega^0 - 2bn$, are evaluated and plotted. Assuming that these frequencies originate in oscillations between a hydrogen atom and the remainder of the molecule, the restoring force residing in the C-H and N-H bonds, the heats of linkage of these bonds are calculated. The method originated by Birge and Sponer for the determination of the heats of dissociation of non-polar, diatomic, gaseous molecules is used. The heats of linkage for a hexane C-H bond is calculated to be 97,000 cal/mol in fair agreement with the 92,500 cal/mol value obtained thermochemically for its homologue, methane. The values for the heat of linkage vary among the different types of molecules, having the relatively high value of 117,000 cal/mol for benzene C-H bonds. The value for the N-H heat of linkage is calculated for one substance, aniline. It evaluates as 113,000 cal/mol and is believed to agree with the 101,000 cal/mol obtained thermochemically for an ammonia N-H bond within the limits of determination of the former value. A possible explanation of the doubleness of the absorption bands observed in the spectra of several substances, notably hexane and cyclohexane, is sought in two types of carbon valence. This doubleness indicates a slight inequivalence in the energy content of two types of C-H bond.

CONSIDERABLE success has been obtained by Birge[1] and others in the evaluation of the heats of dissociation of numerous non-polar, diatomic, gaseous molecules from band spectra data. The method rests upon the classical quantum theory of a quantized anharmonic vibrator and is made possible through the ability of the band spectroscopist to identify and evaluate successive mechanical oscillation frequencies characteristic of the molecule.

The quantum theory predicts the following stationary energy states due to vibration of a diatomic molecule in which the force coefficient varies with the amplitude of the motion:

$$E^n = h\omega^0 n - hbn^2 \tag{1}$$

Here n is a vibration quantum number defining the state, ω^0 the vibration frequency for an infinitesimal amplitude, b a constant arising from the non-linearity in the force law and h Planck's constant. The theory also postulates a series of radiation frequencies

$$\nu^n = \omega^0 n - bn^2 \tag{2}$$

to arise from transitions between these stationary states. Each stationary state has associated with it a mechanical frequency ω^n determined by

[1] Birge, Molecular Spectra in Gases, Bull. Nat. Research Council, 57 (1927).

$$\omega^n = (1/h) \cdot (\partial E^n/\partial n) = \omega^0 - 2bn \tag{3}$$

The maximum vibrational energy which such a molecule can have is

$$E^n_{max} = h \int_0^{n_0} \omega^n dn = h(\omega^0)^2/4b \tag{4}$$

where n_0 designates the limiting stationary state, in which $\omega^n = 0$ and beyond which the molecule dissociates. Putting $\omega^n = 0$ in Eq. (3) gives $n_0 = \omega^0/2b$. $E^n{}_{max}$ is equal to D, the work of dissociation of the molecule. If ν^n and ω^n are measured in spectroscopic frequency units, cm^{-1}, D may be calculated in calories per mol by

$$D = hc(\omega^0)^2 N/4bJ \tag{5}$$

where N is the Avogadro number, J the mechanical equivalent of heat in ergs per calorie and c the velocity of light.

The heats of dissociation for non-polar diatomic molecules, obtained by Birge and others, have been calculated only after successive values of ω^n have been evaluated from the most general types of band spectra and identified with definite values of n. In many instances an expression for ω^n, less simple than that of Eq. (3), including additive terms in higher powers of n, has to be used. Graphically $E^n{}_{max}$ is obtained by plotting values of ω^n against values of n and measuring the area under the curve, the terminals of the curve being ω^0 and n_0 respectively; or rather, by plotting $\omega^{n+1/2}$ against $n+\frac{1}{2}$ since the values of n are obtained from optical data and $\omega^{n+1/2}$ is gotten from

$$\omega^{n+1/2} = \Delta\nu^n/\Delta n = \nu^{n+1} - \nu^n \tag{6}$$

The series of similar absorption bands in the spectra of organic liquids, data for some of which are tabulated in a previous paper,[2] are capable within the limits of experimentation of having their frequencies expressed by the quadratic formula of Eq. (2). This lends support to an hypothesis already advanced by the author that these absorption frequencies originate in anharmonic vibrations within the C-H and N-H bonds. A more definite physical picture of the molecular behavior is the vibration of the hydrogen atom with respect to the remainder of the molecule, the restoring force in the motion originating in the C-H and N-H bonds. Thus, for example, it will be assumed in this paper that the series for benzene arises from changes in vibrational energy of the hydrogen atom with respect to the phenyl radical. It is not assumed that the rest of the molecule represents a rigid structure. The similarities in the infra-red spectra of a large number of compounds indicate, however, that any other vibrations within the absorbing molecule influence the particular series in question only to a minor extent.

The above hypothesis would require that there be an electric moment existing within the chemical bond. That the bond is essentially homo-polar, however, is evident from the fact that the hydrogen atom comes off as an

[2] Ellis, Phys. Rev. **32**, 906 (1928).

atom rather than as an ion. In the analogous case of a diatomic gas molecule it is for those types in which dissociation results in the separation into un-ionized atoms that the equations of the simple forms, (1)–(4) inclusive, are most nearly obeyed.

In Table I are tabulated the wave-lengths, frequencies and their first differences for members of the C-H series of hexane, cyclohexane, benzene,

TABLE I. *Wave-lengths, frequencies and their first differences, for certain organic liquids.*

n	λ	ν^n	ω^n	n	λ	ν^n	ω^n
		Hexane				Cyclohexane	
1	3.42μ	2,925 cm^{-1}		1	3.49μ	2,865 cm^{-1}	
2	1.74	5,750	2,825 cm^{-1}	2	1.75	5,720	2,855 cm^{-1}
3	1.195	8,370	2,620	3	1.20	8,340	2,610
4	0.920	10,880	2,510	4	0.930	10,750	2,420
5	0.749	13,340	2,460	5	0.758	13,180	2,430
6	0.640	15,650	2,300	6	0.648	15,410	2,230
7	0.562	17,800	2,150	7	0.571	17,510	2,100
		Benzene				Chloroform	
1	3.28μ	3,050 cm^{-1}		1	3.32μ	3,010 cm^{-1}	
2	1.68	5,950	2,900 cm^{-1}	2	1.69	5,920	2,910 cm^{-1}
3	1.145	8,730	2,780	3	1.15	8,700	2,780
4	0.874	11,440	2,710	4	0.880	11,350	2,650
5	0.713	14,020	2,580	5	0.721	13,880	2,530
6	0.608	16,430	2,410	6	0.614	16,300	2,420
7	0.532	18,800	2,370				
8	0.476	21,000	2,200				
		Aniline C-H				Aniline N-H	
1	3.25μ	3,075 cm^{-1}		1	2.90μ	3,450 cm^{-1}	
2	1.68	5,950	2,875 cm^{-1}	2	1.50	6,670	3,220 cm^{-1}
3	1.145	8,730	2,780	3	1.03	9,710	3,040
4	0.870	11,500	2,770	4	0.790	12,650	2,940
5	0.712	14,040	2,440	5	0.648	15,420	2,770
6	0.608	16,430	2,390				

chloroform and aniline; and of the N-H series of aniline. In assembling the table the values considered most nearly correct are taken from Table I of the preceding article.[2] In Figs. 1–6 these data are plotted with values of

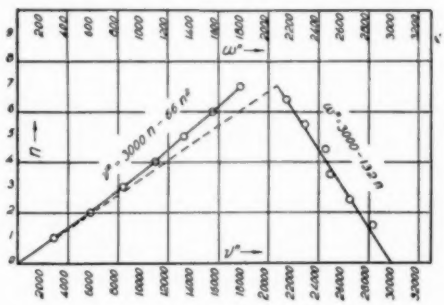

Fig. 1. Hexane.

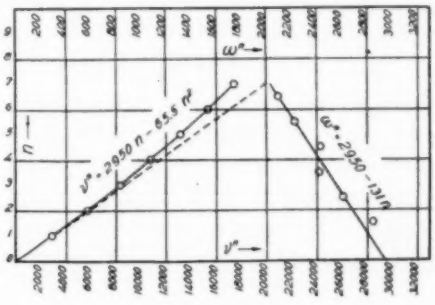

Fig. 2. Cyclohexane.

n as ordinates and values of ν^n and ω^n as abscissas. The upper set of abscissa values are for the mechanical frequencies. The curves to the right and to the left are associated with the ω^n and ν^n values respectively.

Since many of the bands for hexane and cyclohexane were observed as double, a mean wave-length value had to be used. Because of the approximately equal intensities of the components of the latter substance an arithmetical mean was used. The shorter wave-length component of the hexane

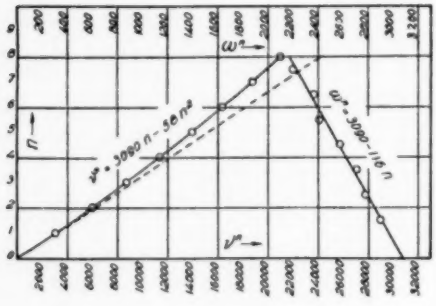

Fig. 3. Benzene.

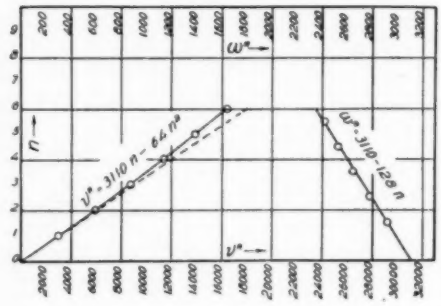

Fig. 4. Chloroform.

bands was more intense than its companion; consequently, a wave-length value was arbitrarily chosen differing from the stronger component by an amount equal to one-third of the separation value.

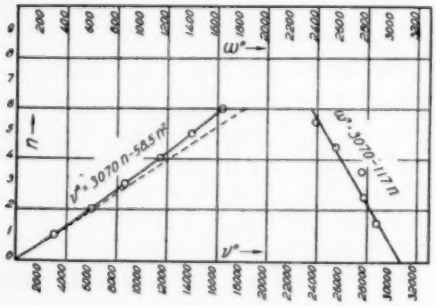

Fig. 5. Aniline C-H

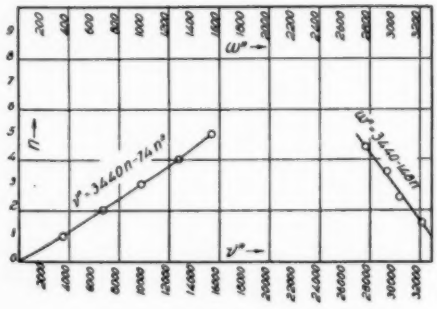

Fig. 6. Aniline N-H

There is no detectable deviation of any optical value from the parabolic curve. The broken line represents the form which the curve would take if the optical frequencies followed a truly harmonic law. This was calculated on the assumption that the frequency of the first series member was accurately determined. The points of the ω^n curve, calculated from the differences in successive ν^n values could scarcely be expected to yield a great degree of accuracy because of the lack of precision in determining the optical values. As mentioned above, ordinate values of $n+\frac{1}{2}$ have been used in the ω^n graph.

The ω^0 and n_0 values were determined from the intercepts of the ω^n curve while the b constant was determined from its slope.

Using the classical quantum[3] theory developed for diatomic gaseous

[3] Although the classical quantum model is used throughout this paper, it is the author's understanding that the conclusions arrived at are equivalent to those which would be obtained from the newer wave-mechanics.

molecules, an attempt has been made to evaluate the heats of linkage, i.e., the heats of dissociation, of the C-H bonds for the five organic molecules listed above and for the N-H bonds of aniline. Eq. (5) has been used for this purpose. As an example of the use of this formula a calculation of D for the benzene C-H bond is shown:

$$D=\frac{6.55\times10^{-27}\times3\times10^{10}\times(3090)^2\times6.06\times10^{23}}{4\times58\times4.186\times10^{7}}=117{,}000 \text{ cal/mol.}$$

Values of ω^0, n_0, b and D are tabulated in Table II. The calculations of D are based upon the assumption that the ω^n curve is linear not only over

TABLE II. *Calculated values of molecular constants for certain organic liquids.*

Liquid	ω^0	b	n_0	D
Hexane	3000 cm^{-1}	66	23	97,000 cal/mol
Cyclohexane	2950	65.5	23	94,000
Benzene	3090	58	27	117,000
Chloroform	3110	64	24	108,000
Aniline C-H	3070	58.5	26	117,000
Aniline N-H	3440	74	23	113,000

the measured range but also over its extrapolated range. It is true that the ω^n values are not accurately enough determined to enable a detection of any possible slight regular deviation from linearity if it exists. The assumption that, even though there should be strict linearity over the lower range of ω^n values, there is no radical deviation from it in the extrapolated region finds its best support in the exact linearity over long ranges in the case of non-polar diatomic molecules.

An attempt has been made to evaluate the accuracy of the measured values of D. This has been done entirely upon the basis of the deviations of the plotted points in the ω^n curves, assuming that Eq. (3) is obeyed throughout the region of extrapolation. In determining the values for the C-H bonds in hexane, benzene, chloroform and aniline it is believed that errors no greater than ±5 percent can arise from inaccurate drawing of the ω^n curves. Possible errors larger than this may arise in the other two instances.

It will be observed that the values of the heats of linkage of the C-H bond vary from 94,000 cal/mol for cyclohexane to 117,000 cal/mol for benzene. This variation lies well outside the limits of experimental determination. The chemist, having only indirect methods of measurement of this quantity, has frequently assumed its equality for all organic molecules.

The best value determined from thermochemical data with which to compare the D values of Table II must be sought in the methane molecule, CH_4. The energy to be associated with each of the four C-H linkages in this molecule may be obtained by taking one-fourth of the result obtained by adding together the heat of formation of methane, the heat of sublimation of carbon and twice the heat of formation of the hydrogen molecule. The

best values obtainable for these are respectively 19,000,[4] 141,000[5] and 105,000 cal/mol.[6] These yield

$$\tfrac{1}{4}(19,000+141,000+2\times 105,000)=92,500 \text{ cal/mol}.$$

Experiments on the heats of combustion indicate that the heat of linkage of the C-H bond is about the same for all members of the paraffine series. Thus we are somewhat justified in comparing the 92,500 cal/mol value determined thermochemically for methane with the 97,000 cal/mol determined optically for hexane, which is a homologue of methane. It is probable that these two values check within the limits of the determinations of the constants involved. Since the contribution of the heat of formation of methane is small, and since the heat of formation of hydrogen is probably quite accurately determined, any appreciable inaccuracy in the chemical determination of D for the methane C-H bonds must be sought in the value of the heat of sublimation of carbon. It is doubtful whether any great accuracy can be assigned to the value quoted for this quantity, inasmuch as values ranging from about 100,000 cal/mol to 287,000 cal/mol are given in the literature. The two most recent determinations are by Ryschkewitsch[7] and Kohn and Gückel.[8] The former obtains a value around 100,000 cal/mol but considers the determination of the latter investigators as the more probable because of the better agreement of their value with that predicted by the Nernst heat theorem.

The optical determination yields a value expressing the energy necessary to remove the first hydrogen atom from the molecule, whereas the thermochemical value is a statistical one. It is entirely probable that this quantity varies with the number of atoms already removed.

The appreciably greater value for the unsaturated molecule, benzene, than for the saturated molecules, hexane and cyclohexane, is of interest. This variation seems reasonable; for, whatever be the nature of the distribution of the valence forces around a carbon atom in the benzene molecule, it would seem that the C-H bond as well as the C-C bonds should be affected by the lack of saturation. The greater value for the bonding force, manifest through the higher value of the fundamental frequency ω^0, and the greater value of the calculated heat of linkage for this molecule seem consistent with the above hypothesis.

It was pointed out in the preceding paper that many of the C-H series members are double. In fact, insofar as the resolving power of the instruments used permit a detection of a separation, it seems that a series is made up of either doublets or singlets throughout. Thus the bands of benzene, chlorobenzene, aniline and chloroform are single, while hexane, cyclohexane, acetone, ethyl acetate and the methyl groups of toluene and m-xylene yield doublets. The singleness of the benzene series and of that characteristic of

[4] Landolt-Börnstein Tables.
[5] Kohn and Gückel, Naturwiss., **12**, 139 (1924).
[6] Bichowsky and Copeland, Jl. Amer. Chem. Soc., **50**, 1315 (1928).
[7] Ryschkewitsch, Zeits. f. Electrochem., **31**, 54 (1925).

the phenyl radical is consistent with the chemist's assertion of the equivalence of the six substitution positions of benzene. This conclusion has also been deduced by Brackett[8] from the relative sharpness of the benzene bands between 0.8μ and 2.6μ as compared with the corresponding bands of the paraffine compounds.

A possible cause for the duplicity of the bands of certain of the compounds is sought in this paper in the inequivalence of the four carbon valencies. Mrs. Lonsdale[9] has made an exhaustive study of the physical evidence indicating such an inequivalence and concludes that there are probably two each of two different types of carbon bond. The difference is geometrical but Mrs. Lonsdale asserts that corresponding physical and chemical differences might be anticipated.

The approximate equality in the intensity of the two components of the doublets of cyclohexane can be accounted for by assuming that successive hydrogenations of benzene involve the bringing into action of identical valence bonds, these being of the type opposite to those of the original benzene linkages.

There seems to be some discrepancy in the ratios of intensities as recorded by different observers for chain hydrocarbons, although the shorter wavelength components always appear with the greater intensity. Thus the record of Meyer, Bronk and Levin[10] of the 3.39, 3.48μ band of hexane[11] shows an intensity ratio of about 3 or 4 to 1. As nearly as can be visually estimated the ratio is at least that great for the higher frequency members of the hexane series determined in this investigation. Barnes and Fulweiler[12] give as a result of a microphotometer determination of the intensities of the two components of the 0.912, 0.932μ (our $n=4$) and the 0.745, 0.760μ (our $n=5$) bands of pentane, and for the corresponding bands for decane and tetradecane, a ratio of 4 to 3. A possible partial explanation for these apparent discrepancies may be found in the fact that isomeric forms may have been present in some of the investigations. Furthermore, the intensity of series members may decrease more rapidly for one component than for its companion.

It has been asserted that the bands of benzene are single. Higher resolution, however, shows that such bands are not monochromatic, but have in themselves a double structure. This is clearly shown in the record of Meyer, Bronk and Levin.[10] Similarly, the components of the bands of the chain compounds show a doubleness within themselves. This type of doubleness is assumed in the present paper to be the fundamental nature of a band arising from vibrational energy changes within a single type of C-H bond.

[8] Brackett, Phys. Rev., **31**, 917 (1928).

[9] Lonsdale, Phil. Mag. **6**, 433 (1928).

[10] Meyer, Bronk and Levin, J.O.S.A. & R.S.I., **15**, 257 (1927).

[11] Although these investigators used hexane in a vapor form, this use of their data seems justifiable on account of the good agreement throughout of the positions of their bands with those determined with liquid hexane.

[12] Barnes and Fulweiler, Jl. Amer. Chem. Soc., **50**, 1033 (1928).

The first, second and fifth series members for toluene and m-xylene are of a three-fold nature; that is, in addition to the strong benzene type of bands there are the weaker doublets which are here credited to the C-H bonds of the methyl groups. This is of interest in connection with toluene, for this molecule may be considered as a phenyl derivative of methane. Although the data are not extensive enough to evaluate the heat of linkage for this type of bond in toluene, its value probably lies between those for benzene and hexane. This estimation is made from the fact that the ω^0 constant is about equal to that of hexane while the b constant, judged from the divergence from linearity among the frequency values observed, more nearly approximates that for benzene. The greater intensity of the shorter wave component for $n=1$ in the curve for toluene by Meyer, Bronk and Levin would permit us to assume that the bonding of a CH_3 group to the phenyl radical always involves the same type of bond, thus leaving within the methyl group two of one type of bond and one of the other. The observations of the present papers upon the second and fifth series members are not accurate enough to permit this interpretation.

It is difficult to reconcile some of the notions of this paper with the usual interpretation of some of the bands of hydrocarbon vapors and gases, for example, the 3.31μ band of methane which has been measured with a spectroscope of high resolving power by Cooley.[13] If it were permissible to identify this band of methane with vibrations between one of the H atoms and the remaining CH_3 group, the effect of increasing molecular weight upon the position of the band could be studied by comparing it with the analogous absorption maxima in higher homologous members of the methane series. From the theory of the quantized anharmonic oscillator there should be an approximately linear relation between the reduced mass of the vibrating molecule and the square of the fundamental frequency arising from these oscillations. Assuming that the 3.31, 3.39 and 3.43μ bands as given by the same observer, Coblentz,[14] arise from oscillations between one of the hydrogen atoms and the remaining alkyl radical, we might expect a linear relation between the squares of the wave-length values and the reduced mass of the vibrator. Table III gives the summarized data in this instance and Fig. 7 shows the resulting approximately linear relationship. The reduced mass here is calculated upon the basis of the mass of the hydrogen atom as unity.

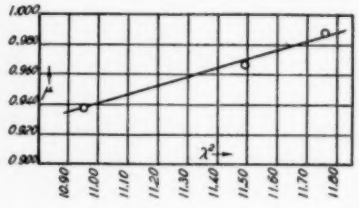

Fig. 7.

If the five percent difference between the value of the heat of dissociation determined thermochemically for a methane C-H bond and optically for a hexane C-H bond represents a true difference, and if the cause for this discrepancy were to be sought in the former determination, one or both of the

[13] Cooley, Astrophys. J., **62**, 73 (1925).

[14] Coblentz, Publication of the Carnegie Institution, **35** (1905).

following two causes, already intimated above, might be suggested: (1) an inaccuracy in the value of the heat of sublimation of carbon used; (2) the fact that the value of the heat of formation of the methane molecule leads to an average value for the heat of linkage of a C-H bond.

TABLE III. *Comparison of reduced mass of vibrator with the square of the wave-length.*

Molecule	Liquid	M_R*	μ	λ	λ^2
Methane	CH_4	15	0.938	3.31μ	10.95
Ethane	C_2H_6	29	0.967	3.39	11.49
Hexane	C_6H_{14}	85	0.988	3.43	11.76

* M_R refers to the mass of the radical on the basis of the mass of the hydrogen atom as unity.

Of the diatomic molecules for which the heat of dissociation has been determined from band spectra data, only one, namely CO, contains a carbon atom. The value of D determined by Birge and Sponer[15] comes out too high. It is of interest to note that a slightly higher value for the heat of sublimation of carbon would bring into good agreement the optically and chemically determined values for both the CO molecule and the hexane C-H bond.

If the above possible discrepancy is to be accounted for on the basis of the statistical nature of the value of the heat of formation of CH_4, it would have to be assumed that successive removals of hydrogen atoms become easier, that is, that the bonding force in a CH molecule is looser than in a C-H bond of the methane molecule. This hypothesis finds some support in considerations of the following paragraph.

Certain electronic bands found at 3900A and 4300A in the spectra of burning hydrocarbons are now fairly definitely assignable to diatomic CH molecules.[16] From measurements upon these bands the value of ω^0 has been approximately determined as 2800 cm^{-1}.[17] Mulliken asserts that the CH molecules emitting these bands must exist in a low-lying energy state rather than in an electronically excited state. This fact makes it justifiable to compare the value of ω^0 for this molecule with that determined for a hexane C-H bond. Applying the equation of a harmonic vibrator, which would hold approximately for the motion with smallest amplitudes,

$$\omega^0=(1/2\pi c)(K/\mu)^{1/2}$$

we get

$$\frac{K_1}{K_2}=\frac{\mu_1(\omega_1^0)^2}{\mu_2(\omega_2^0)^2}=\frac{0.987\times(3000)^2}{0.923\times(2800)^2}=1.23$$

where K_1 and K_2 are the force coefficients for the hexane C-H bond and the CH molecule respectively, ω_1^0 and ω_2^0 the fundamental mechanical frequencies and μ_1 and μ_2 the reduced masses in these two instances. Thus we

[15] Birge and Sponer, Phys. Rev., **28**, 259 (1926).
[16] Mulliken, Phys. Rev., **30**, 785 (1927).
[17] Molecular Spectra in Gases (Ref. 1, p. 230).

see that this calculation leads to a 23 percent greater value for the bonding force for the hexane C-H bond than for the CH molecule.

No great accuracy can be claimed for the calculated value of the heat of linkage of the N-H bond. It will be observed that, in addition to the three bands previously identified by the author as originating in the N-H bond[18] one more has been measured thermally for aniline and a fifth one, found in the records of Russell and Lapraik,[19] has been redetermined in connection with this investigation. The wave-length value for the second member of this series seems upon redetermination to be 1.50μ. The band at 2.8μ identified in Bell's[20] records as the fundamental band of the series seems to be slightly inaccurately located. If it is given the value of 2.90μ found in Bell's later record for diphenylamine[21] it fits the series more accurately. This reassignment of value is partially justified by the fact that the higher series members for both aniline and diphenylamine occupy the same positions in the spectrum. The five optical frequencies yield four values of ω^n, through which the most reasonable straight line has been drawn. This line yields a value of 113,000 cal/mol for the heat of linkage of the aniline N-H bond. An accuracy better than ± 15 percent can scarcely be claimed for this value.

A chemical value can be obtained for this quantity in the case of ammonia, NH_3, by taking one-third of the sum of the heat of formation of ammonia[3] plus one-half of the heat of formation of nitrogen[22] plus three-halves of the heat of formation of hydrogen.[5] This yields

$$\tfrac{1}{3}(12,000+\tfrac{1}{2}\times 268,000+\tfrac{3}{2}\times 105,000)=101,000 \text{ cal/mol}.$$

It is believed that these two values check within the limits of the optical determination. If the higher value determined for aniline does represent a true difference, its larger value might be explained by the increased tightening of the N-H bonds in aniline due to the effect of the unsaturation of the adjoining phenyl radical. That such a tightening does occur is evidenced by the higher frequency values for all of the bands as compared with the corresponding bands of the alkyl amines.

Department of Physics,
Organo-Molecular Investigations,
University of California at Los Angeles,
August 14, 1928.

[18] Ellis, Jl. Amer. Chem. Soc., **50**, 685 (1928).
[19] Russell and Lapraik, Jl. Chem. Soc., **39**, 168 (1881).
[20] Bell, Jl. Amer. Chem. Soc., **47**, 2192 (1925).
[21] Bell, Jl. Amer. Chem. Soc., **48**, 813 (1926).
[22] The average of the optical and chemical values given by Birge and Sponer (Ref. 15) is used here.

THE ABSORPTION SPECTRA OF CERTAIN ORGANIC LIQUIDS IN THE NEAR INFRA-RED

By James W. Sappenfield

Abstract

Absorption spectra have been studied in the region from 0.8 to 2.5μ with an accuracy of 0.002μ for twenty-four organic liquids, including nine alcohols, six esters, two ethers, two aldehydes, and five miscellaneous compounds. The carbon-hydrogen linkage and other similar ones have been discussed as a probable source of the absorption. While certain inconsistencies are pointed out, no other explanation is available. The relative intensity of the various bands has been discussed and it is shown that the bands at 1.4 and 1.0μ and the two bands at 1.2 and 0.9μ evidently arise from different sources. The effect of homology is shown to be slight, which agrees with the conclusions of Weniger. An attempt has been made to get a relation between different band heads of a particular compound. The anharmonic series as suggested by Ellis, and the relation $\nu_n = \nu_0(n)^{1/2}$ suggested by Gapon were both used with moderate success. The latter equation was modified so as to read $\nu_n = \nu_0/(n)^{1/2}$ and applied to part of the data of Weniger with moderate success.

Introduction

During the last several years many investigations have been carried out to determine the relationship of absorption spectra to chemical constitution. These investigations include such work as that of Coblentz[1] and Weniger[2] who studied the region from the visible to 15μ. The region from the visible to 2.5μ has been examined in a number of cases with greater resolving power than that used by Coblentz and Weniger. Work of this kind has been done by Puccianti,[3] Abney and Festing,[4] and Ellis[5] using quartz and glass prisms. Easley, Fenner and Spence[6] have recently studied this region with a grating which gave much better resolution than any of the prisms.

Since there is still not much detailed information available between the visible and 2.5μ, the present investigation was undertaken for the purpose of supplying accurate data on a number of additional organic liquids. In selecting the compounds to be investigated several were chosen from the work of Weniger in order that Weniger's data for wave-lengths greater than 2.5μ might be used in any interpretations that might suggest themselves. In addition to these, several other organic compounds were chosen from different chemical families in order to study similarities and dissimilarities in them.

[1] Coblentz, Investigation of Infra-Red Spectra, Carnegie Inst. Pub. (1905).
[2] Weniger, Phys. Rev., **31**, 388 (1910).
[3] Puccianti, Phys. Zeits., **1**, 494, (1900).
[4] Abney and Festing, Phil. Trans., **172**, (1881).
[5] Ellis, Phys. Rev., **23**, 48 (1924).
[6] Easley, Fenner and Spence, Astrophys J., **67**, 185 (1928).

Apparatus

The spectrometer was specially designed and constructed in the department shop. A diagram is given in Fig. 1. The base $ABCDEF$ was a heavy iron plate mounted on six legs, one at each corner. The mirrors M_1 and M_2

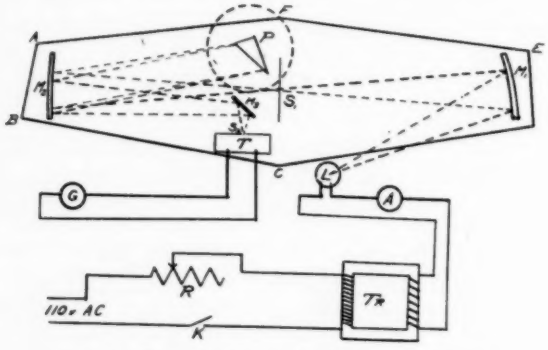

Fig. 1. Diagrammatic sketch of apparatus.

were concave and M_3 was plane. Each of these mirrors was silvered on the front side. The adjustable slits S_1 and S_2 were kept at the same width throughout the investigation; S_1 at 0.10 mm and S_2 at 0.14 mm. The linear thermopile, T, of ten couples of bismuth and silver was made by Coblentz. It was connected in series with a high sensitivity Leeds-Northrup galvanometer. The scale distance used was 4 meters. The glass prism P with an angle of 30° was silvered on the back side and mounted on a high grade divided circle which was divided into divisions of 5 minutes each and could be read accurately to 1 second of arc by a micrometer microscope. The source of radiation, L, was a straight tungsten filament lamp which carried 22 amps. at 11 volts. The power was supplied by a step-down transformer connected to the 110 volt a.c. circuit. Current through the lamp was read on the ammeter A and was regulated by the variable resistance R. A diagram of a cell is given in Fig. 2 in which aa' is a cross section of the circular brass cell; bb' are mica windows, cc' are rubber gaskets and dd' are circular brass rings by means of which the mica windows were pressed against the brass shoulders. The liquid was enclosed in the space e and the entire cell was mounted in a cell holder. Two cells of this kind were mounted, one above the other, in the cell holder. They were identical in construction but one was filled with the liquid under investigation and the other was left empty. The cell holder and a shutter were mounted directly in front of the slit S_1. Six different cell thicknesses were used to bring out the different bands to best advantage. These thicknesses were 40, 10, 5, 2.5, 1.0, and 0.5 mm.

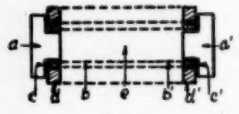

Fig. 2. Absorption cells.

Method

The percentage transmission of the liquid for a particular wave-length was determined by reading the deflection of the galvanometer when the

radiation passed through the full cell and then the deflection when the radiation passed through the empty cell. The ratio of the first of these deflections to the second gives the percentage transmission after multiplying by 100. The corresponding wave-length was determined from the angular position of the prism from which the wave-length could be determined by a calibration curve.

Readings for percentage transmission were taken at intervals of about 15 seconds of arc on the divided circle. This interval amounted to about 0.005μ for the middle of the spectrum. A curve was then plotted on a large scale using percentage transmission as ordinates and angular position of the prism as abscissas. The minimum of the curve was accurately located and the wave-length corresponding to the position of the prism was then determined from the calibration curve. Under normal conditions only one observation was taken for each point on the curve since they could be duplicated to a fraction of a percent.

Calibration

In order to determine the wave-lengths accurately an arbitrary zero position had to be established which could be checked from day to day. A visual observation on the *D* line was finally selected as most satisfactory. This observation on the *D* line was made by a telescope that was focused on the slit S_2. The source of light was a carbon arc cored with sodium chloride. It was substituted for the lamp *L*, Fig. 1.

The absorption bands of chloroform were used for the calibration. Their position was determined as indicated in the preceding section. The angle between these bands and the *D* lines was then plotted against the wave-length of these bands as given by Easley, Fenner and Spence.[6] A smooth curve was then drawn between these points. There were 19 points between 0.589 and 2.28μ and the accuracy was about 0.002μ. The position of the *D* lines was determined at least once a day so that the angle between the various bands and the *D* lines could always be known with certainty. This angle was then used for reading the wave-length from the calibration curve.

Source and Purity of the Liquids

For the most part the materials were obtained from the Eastman Kodak Company and were of the highest purity obtainable. These were iso-propyl alcohol, n-butyl alcohol, iso-butyl alcohol, secondary butyl alcohol, tertiary butyl alcohol, n-propyl amine, n-butyl acetate, n-propyl acetate, pyridine, cyclohexanone, methyl ethyl ketone, n-propyl n-propionate, ethyl-n-butyrate, benzyl methyl ether, benzyl ether, butyraldehyde, and cinnamaldehyde. The chloroform used for calibrating was from Squibb. The ethyl alcohol was marked 99.71 percent pure. The following products were marked "chemically pure": methyl alcohol from the American Chemical Products Company of Rochester, N. Y., and n-propyl alcohol, n-butyl alcohol, iso-butyl alcohol and iso-amyl alcohol from the Coleman and Bell Company of Norwood, Ohio. The methyl acetate was obtained from the General Chemical Company of Easton, Pa., and the ethyl acetate was obtained from

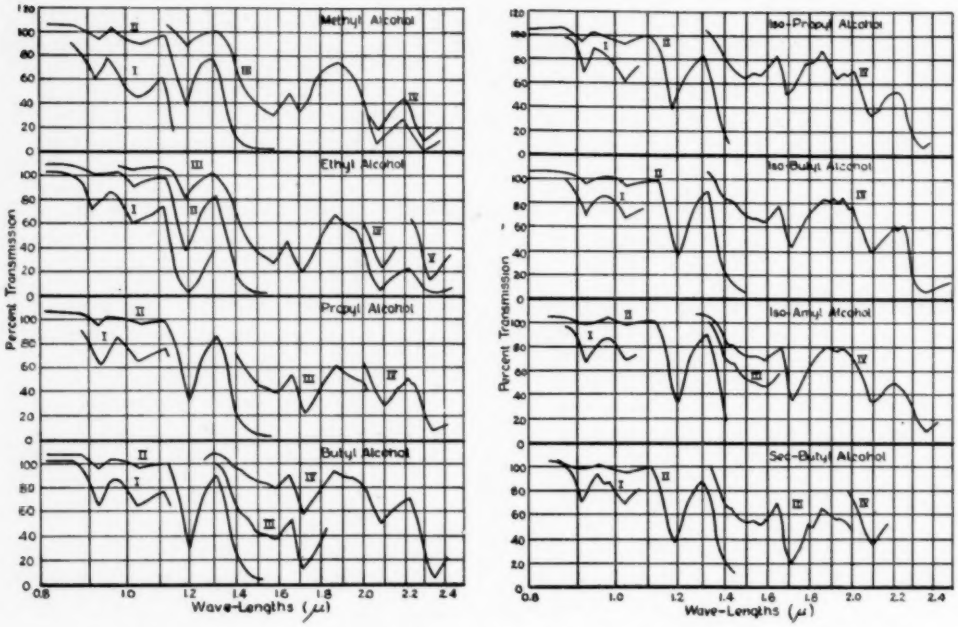

Fig. 3. Percentage transmission in methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, iso-propyl alcohol, iso-butyl alcohol, iso-amyl alcohol and secondary butyl alcohol for cell thickness of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; and V–0.5 mm.

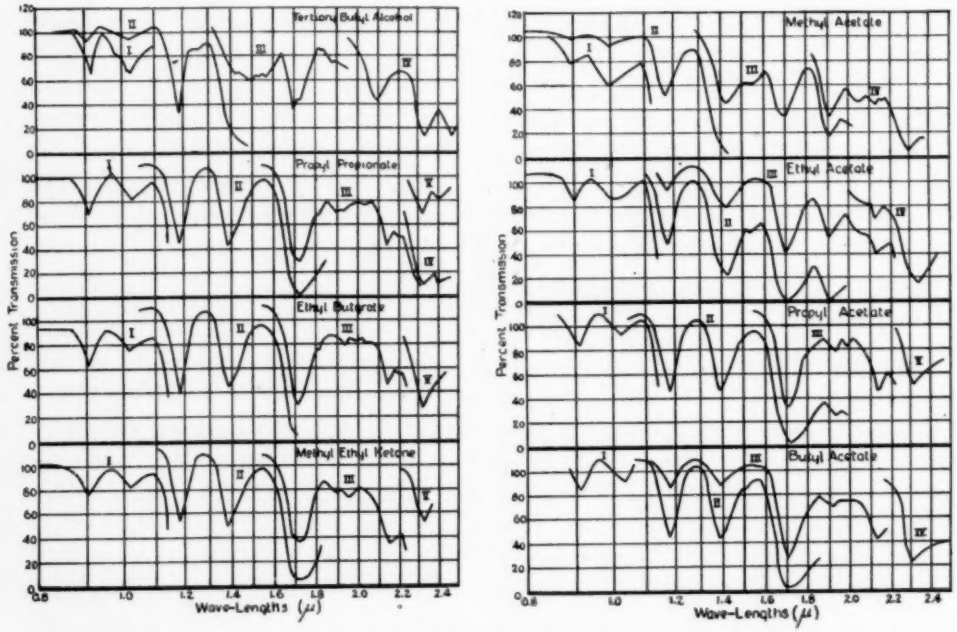

Fig. 4. Percentage transmission in tertiary butyl alcohol, propyl propionate, ethyl butyrate, methyl ethyl ketone, methyl acetate, ethyl acetate, propyl acetate, and butyl acetate for cell thicknesses of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; V–0.5 mm.

the Kauffman-Lattimer Company of Columbus, Ohio. The butyric acid was made by Merck and was marked "Absolute Technical."

Results

A complete curve is given for each of the twenty-four compounds studied. The curves were plotted originally with the angular position of the prism as abscissas and the proper wave-length scale was then superposed but only the wave-length scale has been recorded on these figures.

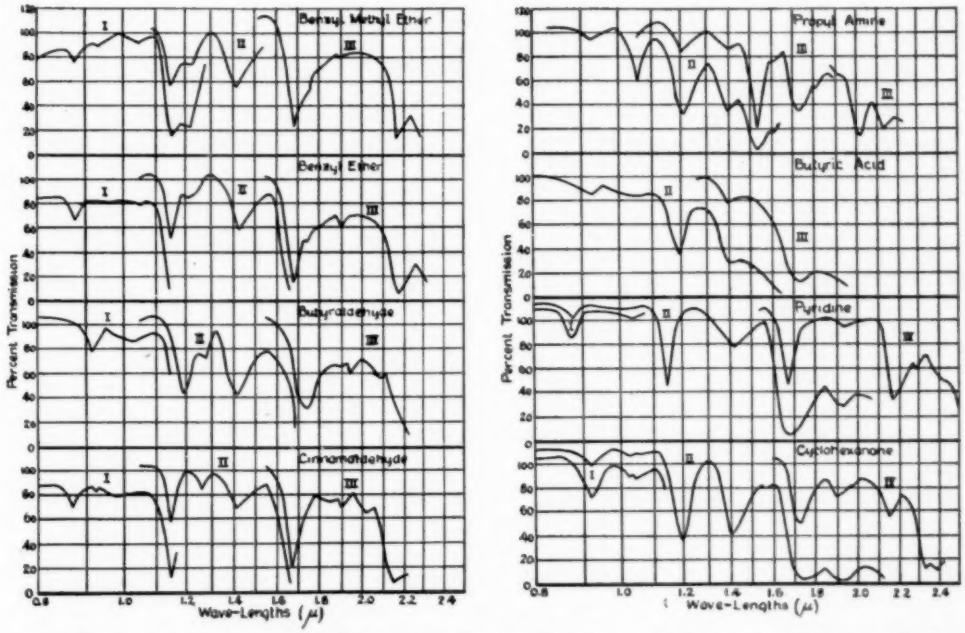

Fig. 5. Percentage transmission in benzyl methyl ether, benzyl ether, butyraldehyde, cinnamaldehyde, propyl amine, butyric acid, pyridine and cyclohexanone for cell thicknesses of I–40 mm; II–10 mm; III–2.5 mm; IV–1.0 mm; V–0.5 mm.

Since the curves are on a very small scale the bands cannot be located from these curves with accuracy. A list of all the bands found between 0.8 and 2.5μ is given in Table I.

The alcohols. This group is composed of nine members, six primary alcohols, two secondary and one tertiary alcohol.

By comparing the curves for the four normal alcohols, one finds certain characteristics developing. The band which appears at 1.4μ is almost completely overshadowed by a band at about 1.55μ. In butyl alcohol a break actually occurs at 1.429μ but in the others this band shows itself only by a broadening of the band. The band at about 1.55μ is broad and shows two definite components except in methyl alcohol when they are both evidently present but unresolved. A band appears at about 1.94μ for all except the methyl alcohol and its intensity increases somewhat with the higher members of the series. Various small bands appear in each.

TABLE I. *List of all observed absorption bands between 0.8 and 2.5μ.*

Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Butyl Alcohol	Iso Propyl Alcohol	Iso Butyl Alcohol	Iso Amyl Alcohol	Sec. Butyl Alcohol
0.916μ	0.886μ	0.923μ	0.923μ	0.910μ	0.918μ	0.918μ	0.912μ
1.030	0.910	1.028	1.032	1.023	1.025	1.030	0.971
1.193	0.939	1.198	1.203	1.187	1.196	1.204	1.029
1.575	1.022	1.529	1.429	1.497	1.412	1.428	1.195
1.707	1.072	1.585	1.533	1.574	1.530	1.528	1.428
2.068	1.190	1.715	1.588	1.698	1.582	1.585	1.505
2.305	1.530	1.949	1.718	1.803	1.714	1.715	1.572
	1.577	2.091	1.931	1.934	1.890	1.931	1.712
	1.711	2.167	2.085	1.984	1.933	2.087	1.766
	1.948	2.232	2.360	2.094	1.967	2.367	1.821
	2.087	2.340		2.125	2.044		1.934
	2.336			2.350	2.085		2.105
					2.218		
					2.372		

Tert. Butyl Alcohol	Propyl Propion-ate	Ethyl Butyr-ate	Methyl Ethyl Ketone	Methyl Acetate	Ethyl Acetate	Propyl Acetate	Butyl Acetate
0.913μ	0.910μ	0.910μ	0.909μ	0.900μ	0.903μ	0.913μ	0.914μ
0.980	1.026	1.020	1.024	1.000	1.012	1.026	1.033
1.022	1.188	1.186	1.183	1.175	1.180	1.187	1.189
1.184	1.389	1.393	1.386	1.442	1.430	1.392	1.396
1.248	1.717	1.718	1.453	1.534	1.538	1.709	1.504
1.421	1.814	1.821	1.727	1.716	1.711	1.790	1.720
1.498	1.937	1.939	1.900	1.921	1.907	1.938	1.929
1.536	2.035	1.989	1.968	2.050	2.061	1.990	2.137
1.574	2.145	2.041	2.163	2.132	2.126	2.140	2.316
1.697	2.209	2.142	2.335	2.173	2.347	2.316	
1.735	2.330	2.201		2.313			
1.830	2.408	2.330					
1.883							
2.100							
2.337							
2.485							

Benzyl Methyl Ether	Benzyl Ether	Butyr-Alde-hyde	Cinnam-Aldehyde	Propyl Amine	Butyric Acid	Pyridine	Cyclo-Hex-anone
0.875μ	0.875μ	0.918μ	0.873μ	0.922μ	0.920μ	0.877μ	0.923μ
0.929	1.052	0.995	0.926	1.055	1.018	1.034	1.024
1.045	1.149	1.033	0.984	1.206	1.190	1.145	1.042
1.143	1.208	1.196	1.030	1.409	1.392	1.428	1.199
1.220	1.428	1.273	1.146	1.534	1.729	1.678	1.417
1.421	1.682	1.418	1.266	1.604		1.937	1.575
1.683	1.747	1.742	1.418	1.729		2.176	1.730
1.759	1.803	1.899	1.683	1.807		2.44	1.907
1.814	1.904	1.943	1.855	1.923		2.56	1.983
1.898	2.176	2.080	1.907	2.025			2.154
2.170			2.022	2.130			2.340
			2.160				2.407

A comparison of the iso-alcohols with the corresponding normal alcohols shows a general, though small, shift toward shorter wave-lengths. In general an iso-alcohol closely resembles the normal alcohol just preceding it in the series.

The secondary butyl alcohol is very much like the iso-butyl alcohol in structure and the absorption curves are very much alike. The tertiary butyl

alcohol is considerably different from the other butyl alcohols in structure since one carbon atom acts as a center and three methyl (CH_3) groups and one hydroxyl group (OH) are attached to it. The absorption curve is different in several respects. An actual minimum occurs at 1.421μ while in the others it was only a point of inflection. The components of the 1.55μ band are much more widely separated than usual. The bands at 1.022 and 1.698μ both appear double but with one component quite weak.

The acetates and related compounds. This group includes four primary acetates, methyl, ethyl, propyl, and butyl, and the related compounds n-propyl n-propionate, ethyl butyrate and methyl ethyl ketone. These liquids show more interesting differences than did the alcohols. The band at 1.92μ which appeared weakly in the alcohols, is one of the major bands in methyl acetate and appears with diminishing intensity in the higher members of the series and is quite small again in the butyl acetate, the propionate and the butyrate. The band at 2.050μ in the methyl acetate is gradually overshadowed and does not show at all in the propyl and butyl acetates although it is present to a small degree in the propionate and the butyrate. The relative intensity of the bands will be discussed later but here it is to be pointed out that the band at 1.4μ decreases rapidly in intensity in passing from methyl acetate to ethyl acetate, decreases less rapidly in passing from ethyl acetate to propyl acetate and remains practically constant in passing from propyl acetate to butyl acetate.

Other compounds. The other compounds were more or less unrelated. The wave-lengths are given in Table I and the curves are shown in the figures. The important characteristics of these curves will be discussed under certain general headings.

Discussion of Results

Chemical bonds and absorption. Probably the most fundamental question that can be asked concerning absorption spectra of this kind is, what is the nature of the absorbing unit. Since a certain set of bands appear in almost all organic materials at approximately the same wave-lengths, it has been assumed that the vibrations take place between certain atoms or atom groups that are common to all these substances. This is obviously a carbon and hydrogen linkage. This viewpoint has been strengthened by such investigations as that by Easley, Fenner and Spence.[6] As halogen atoms are substituted for hydrogen in methane the absorption bands disappear. This seems to show rather conclusively that hydrogen is an essential part of the absorbing system. Ellis has undertaken to show that a C-H bond is the cause of one of the most prominent series of bands in these compounds. He has also found evidence for thinking that N-H[7] and S-H[8] bonds cause characteristic absorption bands. Following this point of view the bands at 1.55μ in the alcohols should be attributed to O-H. This seems reasonable since Weniger's curves show a band at 3.0μ which is the approximate multiple

[7] Ellis, Phys. Rev., 31, 314 (1928).
[8] Ellis, Phys. Rev., 31, 916 (1928).

of the one at 1.55μ. However this is contradicted by the fact that the bands at 1.55μ and 3.0μ do not occur in butyric acid. One may say that the alcohols and acids are quite different chemically but one at least loses some of his confidence in a simple bond theory.

The band at 1.2μ has a very interesting characteristic. In the chain molecules this band is located at about 1.20μ. However the benzene ring derivatives apparently show the same band at 1.15μ. Molecules of combined ring and chain systems may show both bands as shown in the curves of benzyl methyl ether and benzyl ether. The band at 1.15μ is the stronger because the C_6H_5 group is the predominant part of the molecule. This relation is shown in the two aldehydes also. The butyraldehyde is a straight chain molecule and gives the band at 1.196μ. The cinnamaldehyde gives the band at 1.146μ. Since this molecule has only a small chain the absence of the band at 1.2μ is not surprising.

A similar set of conditions arise in the neighborhood of 0.9μ. In the chain molecules the band is at about 0.92μ and in the benzene derivatives it is located at about 0.875μ. In benzyl methyl ether and cinnamaldehyde two bands appear, one at about 0.92μ and the other at 0.875μ with the band at 0.875μ much stronger. In benzyl ether only the band at 0.875μ occurs and in butyraldehyde only the band at 0.918μ is found.

One is not to conclude from this that the difference is entirely between chain and ring formations. Pyridine (C_5H_5N) and cyclohexanone ($C_6H_{10}O$) are both ring molecules. Pyridine gives the typical benzene bands at 0.877 and 1.145μ. Cyclohexanone gives bands at 0.923 and 1.199μ which are characteristic of the regular chain. This fact seems to indicate that the benzene bands are not due to the cyclic arrangement but rather to the C_6H_5 group. This is very possible since this is a very stable chemical group. It should also be mentioned here that bands at 0.878 and 1.153μ appear in chloroform so that bands may be located at these positions without the presence of a benzene ring.

Intensities of bands. The relative intensity of the bands has received very little attention up to the present time. Ellis[9] arranges the bands at 6.9, 3.3, 2.2, 1.7, 1.4, 1.2, 1.0, and 0.9μ in a series and makes the general statement that the intensity decreases with the wave-length with certain exceptions. There are certain cases of relative intensity which seem worthy of consideration. In the first place consider the band at 1.55μ in the normal alcohols. Its intensity remains practically constant in these alcohols. On the other hand its neighbor at 1.71μ grows stronger with each succeeding member of the series. This would indicate that one arises from a part of the molecule which is the same for all members of the series and the other arises from a part that is being altered in passing from one of the normal alcohols to another. These variations in intensity would suggest that the band at 1.55μ is due to an O-H bond and the one at 1.71μ is due to a C-H bond.

[9] Ellis, Phys. Rev., **27**, 298 (1926).

There is reason to suppose that the members of a series of bands should show some kind of consistent relative intensity but there is no such relation for the bands at 1.4 and 1.2μ or at 1.0 and 0.9μ. Furthermore the relative intensity of the bands at 1.0 and 0.9μ may be approximately predicted by knowing the relative intensity of the bands at 1.4 and 1.2μ. It may be said without exception that as the band at 1.4μ decreases in intensity in proportion to the band at 1.2μ the band at 1.0μ decreases in intensity in proportion to the band at 0.9μ. (Compare the curves for methyl acetate, propyl acetate, and pyridine.) If the bands at 1.0 and 0.9μ have about equal intensities, e.g. ethyl acetate, the ratio of intensity of the band at 1.4μ to the band at 1.2μ is about 1.6. If the intensity of the band at 1.4μ is equal to that at 1.2μ, e.g. propyl acetate, the ratio of intensity of the band at 0.9μ to the band at 1.0μ is 1.55. This indicates that the bands at 1.4 and 1.0μ are closely related and that they differ in origin from the bands at 1.2 and 0.9μ.

The variation in intensity of the band at 1.92μ in the acetates is unexplainable. The assumption of a C-H bond or any other kind of bond seems to give negative results. No other kind of explanation is available. Weniger called attention to a similar set of conditions arising in the primary alcohols. A minor band appeared at 4.9μ in methyl alcohol and shifted to longer wave-lengths and faded out until it was not observable in the amyl alcohol. Another band at 5.9μ in the methyl alcohol did the same thing. Weniger offered no suggestions.

Effect of chemical substitutions. Since the absorption spectra of chemically similar compounds are known to be similar, a study of the variations of the spectra of homologous series is interesting. Homologous compounds are compounds which are structurally similar and differ by a CH_2 group. Weniger studied the effects of homology in the primary alcohols, secondary alcohols, certain acids and esters. He concluded that in ascending the series in the alcohols several of the bands shifted to longer wave-lengths; in the esters the effect was very slight. His conclusions are both verified for bands between 0.8 and 2.5μ. In the alcohols there seems to be a general tendency toward a shift to longer wave-lengths although it is quite small. In the acetates, which are a class of esters, there seems to be no general systematic changes.

Ethyl acetate differs from propyl propionate by an additional CH_2 in both the acid and basic parts of the molecule. The result is a general shift to longer wave-lengths except the band at 1.430μ shifts to 1.398μ and the band at 2.347μ shifts to 2.330μ.

Butyl acetate, propyl propionate and ethyl butyrate have the same molecular weight and general formula. The structure of one may be changed into the next by transposing a CH_2 group from the acid part of the molecule to the basic part. The shifts are all quite small and are not consistent in the two transformations available for consideration.

Ethyl acetate ($CH_3COOC_2H_5$) differs in structural formula from methyl ethyl ketone ($CH_3COC_2H_5$) by one oxygen atom in the central chain. This

change in structure results in a shifting of the bands to longer wave-lengths except the band at 1.430μ shifts to 1.386μ and the band at 2.347μ shifts to 2.335μ.

Theoretical Discussion

It seems probable that the different bands of a compound should be related and that their position might be expressed by an equation. Kratzer[10] developed the theory of the anharmonic oscillator and Ellis has applied it to his data. Kratzer showed that $\nu_n = n\nu_0(1-nx)$ or $\nu_n = An - Bn^2$ where x, A and B are constants, n is an integer, ν_n is the frequency of the band and ν_0 a fundamental frequency. Ellis[9] originally used the frequency of the band at 6.8μ as the fundamental but he recently[7] revised it and used the band at 3.3μ.

Gapon[11] suggested the equation $\nu_n = \nu_0(n)^{1/2}$ where ν_n was the frequency of the band, ν_0 the fundamental frequency, and n an integer. In applying this equation the author noticed that the equation $\nu_n = \nu_0(n)^{-1/2}$ gave results that agree with the bands recorded by Weniger. In both cases the ν_0 was the frequency of the band at about 3.3μ.

Table II.

Butyl Alcohol							*Ethyl Acetate*						
Wave-lengths $\lambda_n = 3.415n \pm 1/2$			Wave-numbers $\nu_n = 2964n - 63n^2$			Wave-length	Wave-lengths $\lambda_n = 3.390n \pm 1/2$			Wave-numbers $\nu_n = 3074n - 77n^2$			Wave Length
λ Obs.	n	λ Calc.	ν Obs.	n	ν Calc.	λ Calc.	λ Obs.	n	λ Calc.	ν Obs.	n	ν Calc.	λ Calc.
0.923μ	14	0.913μ	10834.2	4	10848	0.922μ	0.902μ	14	0.906μ	11074	4	11056	0.904μ
1.032	11	1.030					1.012	11	1.022				
1.203	8	1.217	8312.6	3	8325	1.201	1.180	8	1.199	8475	3	8523	1.173
1.429	6	1.394					1.430	6	1.384				
1.533	5	1.527					1.538	5	1.516				
1.588							1.711	4	1.695	5845	2	5836	1.713
1.718	4	1.708	5820.7	2	5676	1.762	1.907	3	1.957				
1.931	3	1.972					2.061						
2.085							2.126						
2.360	2	2.415					2.347	2	2.397				
3.0							2.65						
3.5	1	3.415	2857.1	1	2901	3.45	2.8						
4.9	2	4.83					3.05						
5.6							3.45	1	3.390	2899	1	2995	3.389
5.8	3	5.91					4.3						
6.1							4.95	2	4.8				
6.9	4	6.82					5.35						
7.2							5.85	3	5.87				
7.45	5	7.63					6.6	4	6.78				
7.75							7.3	5	7.6				
8.0							8.1	6	8.3				
8.45	6	8.35					8.9	7	9.0				
9.15	7	9.04					9.7	8	9.6				
9.45							10.05	9	10.2				
9.6	8	9.65					10.50						
10.0	9	10.25					10.75	10	10.7				
10.5		10.8					11.05	11	11.25				
11.3	11	11.3					11.8	12	11.75				
11.8	12	11.8					12.2	13	12.2				
12.0							12.7	14	12.7				
12.15	13	12.3					13.8	16	13.6				
12.45													
12.8	14	12.8											
13.1	15	13.2											
13.5	16	13.65											
13.8													

The calculated results from these equations are given in Table II for butyl alcohol and ethyl acetate. In making the calculations ν_0 was deter-

[10] Kratzer, Zeits, f. Physik, 3, 289 (1920).

[11] Gapon, Zeitz. f. Physik. 44 600 (1927).

mined by substituting known values of ν_n and n in the equation $\nu_n = \nu_0(n)^{1/2}$. The agreement between calculated and observed values is about the same in the other compounds studied in this investigation. In each case the agreement is fair but in no case is it nearly perfect. The square root relation has the advantage of fitting many more bands but it lacks the ease of physical interpretation that comes in case the molecule is considered as an anharmonic oscillator. While other series of a similar nature suggest themselves they are not nearly so long and the accuracy is not good. It is recognized that these suggestions are purely empirical.

In conclusion the author wishes to express his appreciation to Professor Alpheus W. Smith for suggesting the problem and for his advice and assistance in the work. He is also indebted to Professor C. E. Boord and Dr. R. K. Summerbell for advice on the chemical part of the work.

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September 20, 1928.

COMBINATION FREQUENCIES OF THE INFRA-RED BANDS OF QUARTZ

By E. K. Plyler

Abstract

Many observers have studied the infra-red absorption bands of quartz and have found regions of intense absorption at 9μ, 12.5μ, 20μ and 26μ. These regions of absorption are assumed to be the fundamental frequencies of quartz. By combining these assumed fundamental frequencies six bands in the region from 3μ to 9μ are accounted for. Also the writer has experimentally located two bands at 2.72μ and 3.18μ which have not been previously observed. The frequencies of these two bands agree with two combinations of the fundamental frequencies. This gives a total of eleven absorption bands for the ordinary ray of quartz, extending from 2.72μ to 26μ whose frequencies agree, with only small differences, with the calculated values.

Introduction

THE infra-red absorption of quartz has been studied by several investigators. There have been found bands due to the absorption of the ordinary ray and the extraordinary ray but only bands due to the ordinary ray have been considered in this work. Schaefer, Bormuth and Matossi[1] have shown that there exists many combination bands in $CaCO_3$ and in other carbonates. In the present work the same method has been applied to the infra-red bands of quartz. Four intense bands of quartz are assumed to be the fundamental bands and other bands are calculated by simple combinations of the fundamental frequencies. A comparison is then made between the wave-lengths of the calculated bands and observed bands. Some simple combinations of the fundamental frequencies indicated that there might be several bands, yet unobserved, in the near infra-red and the writer has made a study of this region to see if they were present.

Experimental Procedure in Present Work

A Hilger quartz spectrometer for the infra-red was used as the resolving instrument. The high resolution was an advantage, but the absorption by the prism in the region from 2.9μ to 3.10μ caused the deflections of the galvanometer to be small. The new bands which were found did not fall in this region so that this did not prove a disadvantage. Globar was used for the light source and it was found that the deflections of the galvanometer were about three times as great as for a Nernst glower. The detecting system was made up of a Hilger thermopile and a galvanometer of a sensitivity of 10 mm per microvolt.

The thermopile was well wrapped and isolated and the galvanometer was placed on a pier not connected to the floor. At times the galvanometer showed some unsteadiness which at first was attributed to its high sensitivity. However, upon investigation it was found that the galvanometer was steady

[1] Matossi, Zeits. f. Physik 39, 648 (1926).

when placed in a closed circuit with the same resistance as the thermopile resistance. The unsteadiness of the galvanometer when connected with the thermopile was due to small adiabatic changes in the air of the room. By suddenly opening a door in that part of the building a deflection was obtained in one direction and closing the door would give a deflection of the galvanometer in the opposite direction. On using a flourite window over the thermopile slit and making all openings to the thermopile chamber air tight, the fluctuations of the galvanometer ceased.

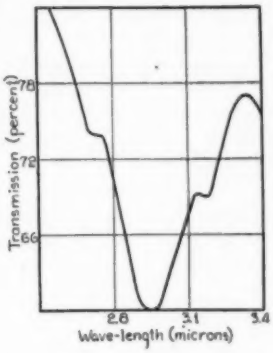

Fig. 1. The infra-red absorption of quartz for a section 3 mm thick cut perpendicular to the optic axis.

Results of Present Experimental Work

The absorption for a piece of quartz cut at right angles to the optic axis is shown in Fig. 1. The specimen was 3 mm thick. The readings were made at intervals of 0.01μ and the slit width of thermopile included about 0.015μ in this region. An absorption band was found at 2.72μ which is probably a part of the more intense band at 2.96μ. The band at 2.96μ is complex and has been studied by Dreische[2] who found three maxima at 2.91μ, 2.97μ and 3.02μ. Another band of small intensity has been observed by the writer at 3.18μ.

Summary of Work of Previous Investigators

The bands at 2.72μ, 2.96μ and 3.18μ as found by the writer will now be used in connection with the work of Rubens,[3] Nichols[4] and Coblentz[5] to study the frequency combinations of the infra-red bands of quartz. Coblentz has studied the region from 2μ to 6μ and found that at 3.5μ the absorption began increasing rapidly. A band was observed at 4.35μ which is shown in Fig. 2, curve *A*. Merritt[6] has also studied the infra-red absorption of quartz for this region and he found small bands at 3.75μ and 4.10μ. Dreisch has recently studied the absorption of quartz and observed a band at 3.75μ.

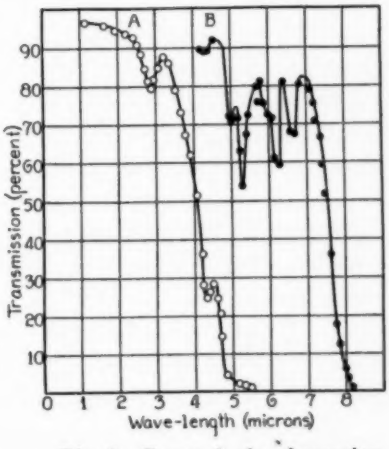

Fig. 2. Curve *A*, the absorption spectrum of quartz as observed by Coblentz. Curve *B*, the absorption spectrum of quartz to 8μ as observed by Nichols.

In Fig. 2, curve *B*, the absorption bands of quartz for the ordinary ray are shown as observed by Nichols. The absorption of quartz is large in the region from 4.5μ to 8μ and it was necessary to use a very thin section.

[2] Dreisch, Zeits. f. Physik **42**, 426 (1927).
[3] Rubens, Preuss. Akad. Wiss., Berlin **16**, 198 (1919).
[4] Nichols, Phys. Rev. **4**, 297 (1897).
[5] Coblentz, Investigations of Infra-Red Spectra, Part 3, p. 21.
[6] Merritt, Phys. Rev. **2**, 424 (1894).

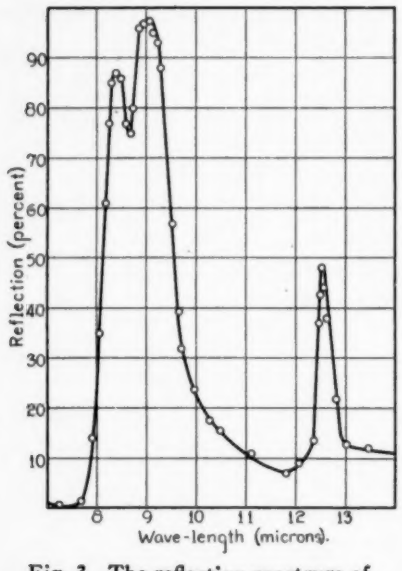

Fig. 3. The reflection spectrum of quartz observed by Coblentz.

In Fig. 3 are shown the reflection spectra of quartz from 8μ to 14μ as observed by Coblentz. Nichols found that although the thickness of his specimen was only 0.18 mm, he was not able to obtain any transmission beyond 8μ.

Bands were observed at 8.40μ, 9.00μ and 12.5μ. Rubens has found that two selective bands of quartz are located at 20.5μ and 26μ.

Interpretation of Observed Bands

Eleven bands have been observed in the infra-red spectra of quartz for the ordinary ray. The four bands at 9.00μ, 12.5μ, 20μ and 26μ are assumed to be fundamental bands. This assumption is made on the basis of the great intensity of the bands and their position in the spectrum. By the theory of band spectra each band observed must be a fundamental, a harmonic or a combination band. The intensity relations, which are very helpful in the study of combinations, have not been studied closely. This was not possible as all of the fundamental bands have been observed by reflection. The existence of other bands of small intensity agreeing with other combinations of the fundamental frequencies is likely, but the intensity is probably small and in some cases is concealed by some of the stronger bands. In many cases several combinations would agree with an observed band to within the limits of error, but the simplest combination was always chosen as it was thought this would be the most intense.

In Table I are given the wave-lengths of the observed and the calculated bands and the combination which is thought to have produced the bands. Also the frequencies of the calculated bands are given.

The band at 9μ, which is assumed to be one of the fundamental bands, and is designated ν_1, has a weaker component at 8.40μ. When there is a band which may be identified with a combination including ν_1 there should be two components of the band. Some of the combination bands including ν_1 have two components, but others do not. For example, only one component of the band, which is identified with the combination $2\nu_1+\nu_2$, has been observed. The other component of $2\nu_1+\nu_2$ should probably be less intense and is probably overlapped by the stronger band at 2.96μ.

Other combinations, which have not been included in Table I, point to the existence of many bands of small intensity. The reason that they do not appear is likely because these bands may be concealed in the stronger bands observed or the combination may have zero intensity. In addition to experimental errors there are other factors which should be considered

TABLE I. *Observed and calculated absorption bands of quartz.*

Obs. Band	Cal. Band	Combination	Wave-Number	Obs. Band	Cal. Band	Combination	Wave-Number
2.72μ	2.80μ	$3\nu_1$	3570cm^{-1}	6.00	5.96	$\nu_1+\nu_3$	1678
2.96	3.00		3333	6.26	6.26		1599
3.18	3.14	$2\nu_1+\nu_2$	3180		6.25	$2\nu_3$	1600
	3.33		3022				
	3.55	$2\nu_1+\nu_3$	2868		6.35	$\nu_1+\nu_4$	1575
	3.69		2710	6.65	6.68		1496
3.75	3.62	$2\nu_1+\nu_4$	2765	8.40	8.40	ν_1	1190
	3.84		2607	9.00	9.00		1111
4.10	4.20	$2\nu_1$	2380	12.5	12.5	ν_2	800
4.35	4.50		2222				
5.02	5.02	$\nu_1+\nu_2$	1994	20.5	20.5	ν_3	488
5.30	5.23		1911	26	26	ν_4	385

in giving the reason for the variation of the observed and calculated bands. In the first place the wave-lengths of all the assumed fundamental bands have been observed by reflection and the wave-lengths of the combination bands and harmonics have been observed by absorption. Secondly, the calculated values of $2\nu_1$ and $3\nu_1$ and all combinations including $2\nu_1$ should have a correction factor. Kratzer[7] has shown that the ratio of the frequencies of the fundamental and successive overtones should be

$$\nu_0(1-x) : \quad 2\nu_0(1-2x) : \quad 3\nu_0(1-3x)$$

This correction has not been made because it would probably not be accurate due to the large errors in the observed value of ν_1. We would expect to find differences between the observed and calculated bands.

UNIVERSITY OF NORTH CAROLINA,
May 6, 1928.

[7] Kratzer, Zeits. f. Physik **3**, 289 (1920).

ARCS WITH SMALL CATHODE CURRENT DENSITY

By J. Slepian and E. J. Haverstick

Abstract

Arcs with cathode current densities of less than one hundred amperes per cm², have been found to exist at gas pressures of from 10 to 50 mm. The theory that electrons are drawn from the cathode by intense electric fields maintained by space charges cannot apply to these arcs.

TO ACCOUNT for the electric arc with cold cathode, that is, with a cathode whose temperature is so low that thermionic emission from it contributes only negligibly to the arc current, it has been proposed[1] that electrons are drawn from the cathode by a very intense electrostatic field at the cathode surface, this field being set up by the positive space charge sheath which forms next the cathode. An important consequence of this view is that cold cathode arcs should not be able to exist with less than a minimum cathode current density of considerable magnitude. This may be seen as follows.

To draw electrons from a cold cathode surface requires gradients in excess of 10^6 volts per cm so that a lower limit to the electric field is established. This fixes the total space charge in the space charge sheath since this must be proportional to the field. The field and space charge being given, the positive ion current density is substantially determined by the further limitation that the total potential drop in the space charge sheath is the cathode drop for the arc. The total arc current density must be at least as large as this positive ion current density. Proceeding quantitatively, we have, if the thickness of the space charge sheath is less than the mean free path of a positive ion, and the space charge neutralizing effect of electrons is neglected, for the positive ion current density I_p the equation of Langmuir[2]:

$$I_p=(0.543\times10^{-7})V^{3/2}/M^{1/2}x^2 \tag{1}$$

where x is the distance in cm in the space charge sheath measured from the side remote from the cathode, V is the potential in volts at point x, and M is the molecular weight of the positive ion. This gives for the gradient at the cathode surface:

$$I_p=\left(\frac{3}{4}\right)^{3/2}(0.543\times10^{-7})\frac{(\partial V/\partial x)^{3/2}}{M^{1/2}d^{1/2}} \tag{2}$$

d being the thickness of the space charge sheath. If the electric gradient at the cathode surface is to be greater than 10^6 volts/cm we must then have:

$$I_p>35.5/M^{1/2}d^{1/2} \tag{3}$$

On the other hand the cathode drop V_c from (1) is:

$$I_p=(0.543\times10^{-7})V_c^{3/2}/M^{1/2}d^2 \tag{4}$$

[1] Langmuir, Zeits. f. Physik **46**, 282 (1927).

[2] Langmuir, G. E. Rev. **26**, 732 (1923).

Hence,

$$d=(2.33\times10^{-4})V_c^{3/4}/M^{1/4}I_p^{1/2} \tag{5}$$

Substituting in (3) we get:

$$I_p>2320I_p^{1/4}/M^{3/8}V_c^{3/8} \tag{6}$$

and this reduces to:

$$I_p>30,800/M^{1/2}V_c^{1/2} \tag{7}$$

If the molecular weight of the ion is less than 40, and the cathode drop less than 20 volts, I_p will be greater than 1090 amperes per cm². Unless the ions are of greater molecular weight than 40, it should not be possible to have an arc with less than 1000 amperes/cm² at the cathode.

Some time ago, one of the authors observed that when the space between electrodes in a vacuum tube at a pressure of a few cm was broken down by sufficient voltage from a direct current generator capable of delivering twenty amperes or more, an arc formed almost immediately, that is a discharge requiring less than fifty volts to be maintained. Furthermore, he found that this arc could burn for several seconds before melting of the electrodes would occur. From this he concluded that the current density in the arc must be small.

Because of the importance of this result in relation to the theory just outlined it was thought desirable to repeat this experiment and to make observations on the current density in the discharge. Accordingly 9 tubes were made up, each with two electrodes. The anodes in these tubes were of 0.318 cm diameter tungsten rod, and the cathodes were rectangular parallelopipeds $2.5\times1.0\times0.8$ cm of various materials. Two tubes were also made with both electrodes of nickel rod, 0.45 cm diameter and 2.8 cm long. The various tubes were filled with argon, neon, and hydrogen at the pressures indicated in Table I. The test on each tube consisted in placing it in series with an open switch in a 500 volt direct current circuit, with enough resistance to limit the current to 25 amperes. On closing the switch, a discharge would generally start through the tube, and an oscillogram of the current and voltage of the tube, and a photograph of the discharge was taken. A switch in parallel with the tube was arranged to close and short-circuit the tube 0.06 seconds after the discharge started. In some cases, when the discharge did not start at 500 volts, the tube was made to glow by the proximity of a Tesla coil, and then the discharge would take place upon the application of the 500 volts.

From the oscillogram it was verified that the discharge had the form of an arc, i.e., that the voltage was low, and the current was measured. The area on the cathode covered by the arc was estimated from the marking on the cathode, and from the photograph. The results are given in Table I.

The cathode current densities shown in the table vary somewhat erratically but they are all very decidedly less than 1000 amps/cm². In these arcs then the theory that electrons are liberated from the cathode by space-charge sheath-gradients greater than 10^6 volts/cm seems to be untenable.

During the period of exposure of the camera, and the duration of the arc, 0.06 seconds, there was undoubtedly some motion of the arc over the cathode surface. This would cause the areas observed to vary erratically, and make

TABLE I. *Data for the arcs.*

Tube No.	Cathode metal	Gas	Pressure (mm)	Arc area on cathode (cm^2)	Current in arc (amps.)	Voltage of arc	Current density at cathode ($amps/cm^2$)
1	Al	Ne	24	3.1	22.5	30	7.2
7	Al	Ne	24	3.1	23.8	30	7.6
6	Al	Ne	12	3.1	25.0	20	8.0
3	Al	A	12	3.1	22.5	20	7.2
4	Al	A	30	0.95	25.0	20	26.0
5	Zn	A	30	0.50	25.0	20	50.0
8	Ni	A	12	0.20	25.0	20	125
9	Ni	A	35	0.38	25.0	20	66
2	W	A	24	0.78	25.0	20	32
10	Al	H_2	48	0.8	17.8	82	22.2
11	Al	H_2	48	0.6	18.6	62	31.0

the calculated current densities of the table too low. It might perhaps even be argued that there was sufficient motion during the arcing period to make an actual current density of 1000 $amps/cm^2$ consistent with the areas observed. However, 25 amperes at this current density would cover a circular spot 1.8 mm in diameter, and if the larger cathode area was covered by the motion of such a spot we should expect to find trails of this width on the cathode. However, there is no evidence of such a trail structure in the markings on the cathodes.

To test this matter further some pictures were taken of the discharge with a moving picture camera taking 128 pictures per second. These pictures showed that there was motion of the discharge during the 0.06 seconds, but that the maximum error in the area determination of the table was probably not over 100 percent, so that actual current densities might be twice those shown in Table I.

It appears then that the high cathode gradient theory of the arc is inapplicable to arcs at moderately low pressures because of the low current density. One of the authors has pointed out[3] that at atmospheric pressures if the layer of gas next to the cathode is sufficiently highly ionized, all the arc current can be carried to the cathode by the positive ions, so that an electron current from the cathode is unnecessary. It is interesting then to find that the cathode current density decreases with pressure, so that it is still possible for positive ions to carry the whole current. If the cathode current density remained high, as at atmospheric pressures, more than 100 percent ionization would be necessary to supply enough positive ions to carry the current. The suggestion was also made that the gas layer next to the cathode might be kept highly ionized by being maintained at a very high temperature, and calculations showed that the electrical energy input into this layer was more than enough to keep it hot. Similar calculations made with these low pressure, low current density arcs lead to entirely similar conclusions.

RESEARCH DEPARTMENT,
W. E. & M. Co., E. PITTSBURGH, PA.
September 26, 1928.

[3] Slepian, Phys. Rev. **27**, 407 (1926).

THE BEHAVIOR OF GLASS AS A DIELECTRIC IN ALTERNATING CURRENT CIRCUITS: II. THE EFFECT OF FREQUENCY AND OF TEMPERATURE UPON THE POWER LOSS

By Louise S. McDowell and Hilda L. Begeman

Abstract

Power factor, power loss per unit applied potential difference, and capacitance, for six glasses, at several constant temperatures, with frequency varying from 800 to 4000 cycles per sec. and for one glass with frequency varying from 100 to 1500 kilocycles per sec.; power factor of one glass at constant frequency of 1000 cycles per sec. with temperature varying from 30°C to 160°C and at −186°C.—Curves show $\log P/E^2$, $\log \tan \phi$, and $\log C$ respectively as functions of $\log f$; C as function of $C \tan \phi$ and $\log \tan \phi$ as function of temperature. For the audio frequency range, results fit equation $P/E^2 = C\omega \tan \phi = \text{const} \times f^n$ at all temperatures investigated; for the radio frequency range, $\tan \phi$ is found to reach a minimum at about 700 kilocycles and to increase rapidly at higher frequencies; capacitance decreases with increasing frequency throughout the entire range. The exponent n is found to decrease slightly with increase in temperature. At the constant frequency of 1000 cycles the variation of power factor with temperature for one glass fits the empirical equation, $\tan \phi = 0.0077T$. The results are compared with those of previous investigators. For the audio frequency range they are shown to accord with the von Schweidler equations and not to give the maximum value of $\tan \phi$ to be expected from the theories of Wagner and Joffé. On the assumption that the exponent n is to be identified with the exponent of the time factor in the equation for the absorption current, $i = \beta C_0 E t^{-n}$, von Schweidler's equations are thrown into a form which permits the calculation of n, β, and C_0, the geometrical capacitance, from the variation of capacitance with frequency. Values of n, β and K_0, the dielectric constant, so calculated are given. It is suggested that the rapid increase in power factor at frequencies above 700 kilocycles may indicate another cause of power loss effective only at higher frequencies. As a further test of Joffé's theory, values of the apparent parallel resistance of one condenser, calculated by extrapolation from power loss measurements for a frequency of one-sixtieth of a cycle per sec. are compared with the d.c. resistance at approximately 30 seconds after application of the e.m.f. Agreement is fair.

THE purpose of the investigation was to compare the variation with frequency and temperature of the power loss and power factor of glass as experimentally determined, with the law of variation to be expected from the several theories. The glasses used were the six described in Part I,[1] of widely different power factor. Measurements of power factor, power loss, and capacitance were made: (1) at several constant temperatures with frequency varying from 800 to 4000 cycles per sec.; (2) for one glass at room temperature with frequency varying from 100 to 1500 kilocycles per sec.; (3) with varying temperature at the constant frequency of 1000 cycles per sec.

[1] L. S. McDowell and H. Begeman, Phys. Rev. **31**, 476 (1928).

Methods of Measurement

As in Part I measurements of equivalent series resistance and capacitance were made by means of a capacitance bridge. The test condensers with mercury electrodes, previously used, were placed in an electric furnace. During measurements the heating current was stopped and the heating coil grounded to prevent the effects of stray capacitance between the outer electrode and the coil. The temperature was measured either by a mercury thermometer dipping into the mercury of the inner electrode or by a thermocouple in conjunction with a potentiometer. For the measurements at constant frequency and varying temperature a condenser was made from a "Pyrex" test-tube. The test-tube, 30 by 2.5 cm, was coated inside and out with gold applied as in china painting and fired at a temperature of 660°C. Several coats were applied until the resistance between bands clamped at top and bottom was only a few tenths of an ohm, yet the coating was so thin and so firmly adherent as to insure good contact throughout the entire range of temperature. Contact to the external electrode was made by three encircling copper bands held in contact by screws, nuts and spiral steel springs; contact to the inner electrode by three bands of spring steel, gold plated, bent into the form of cylinders and sufficiently stiff to hold firmly.

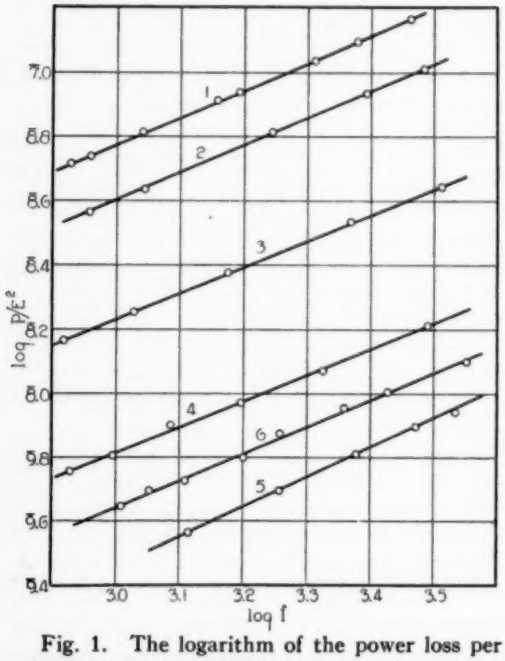

Fig. 1. The logarithm of the power loss per unit applied potential difference as a function of the logarithm of the frequency.

The tangent of the phase difference, $\tan \phi = R\omega C$, was calculated from the measured values of equivalent series resistance, R, and capacitance, C. Since for small values of the phase difference, $\tan \phi \approx \sin \phi = \cos \theta$, the power loss per unit applied potential difference, P/E^2, was calculated from the relation $P = EI \cos \theta \approx E^2 \omega C \tan \phi = E^2 R \omega^2 C^2$.

The Effect of Frequency

Fig. 1 shows the logarithm of the power loss per unit applied potential difference plotted as a function of the logarithm of the frequency. Within the experimental errors the lines are straight and therefore fit the equation

$$\log P/E^2 = \text{const.} + n \log f \tag{1}$$

or

$$P/E^2 = C\omega \tan \phi = \text{const.}\ f^n \tag{2}$$

From Eq. (2) it is evident that

$$C \tan \phi = \text{const.}/f^{1-n} \tag{3}$$

or

$$\log C \tan \phi = \text{const.} - (1-n) \log f \tag{4}$$

If the variation in capacitance with frequency is negligible then

$$\log \tan \phi = \text{const.} - (1-n) \log f \tag{5}$$

Fig. 2 shows the resulting lines to be straight within experimental errors. Actually the variation in capacitance with frequency was slight and appeared to follow a similar law

$$\log C = \text{const.} - p \log f \tag{6}$$

as indicated in Fig. 3.

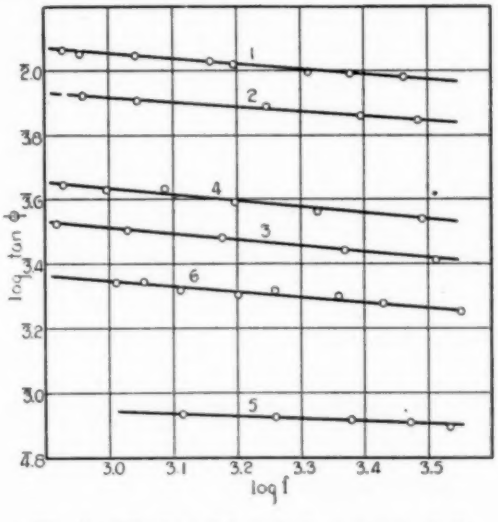

Fig. 2. The logarithm of the tangent of the phase difference as a function of the logarithm of the frequency.

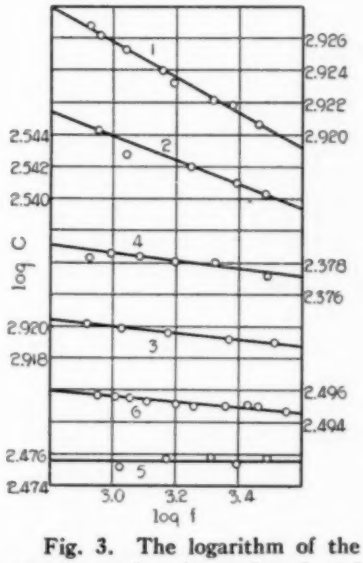

Fig. 3. The logarithm of the capacitance in $\mu\mu$f as a function of the logarithm of the frequency.

In interpreting the results three theories of dielectric absorption were considered; the theory of Maxwell based on inhomogeneities of structure, as amplified and extended to the alternating current phenomena by Wagner; the Pellat-von Schweidler theory based on molecular lag in following the field; and the theory of Joffé based on electrolytic polarization. Wagner's theory leads to the exponential equation for the absorption current as a function of time

$$i = Ae^{-t/T} \tag{7}$$

and to expressions for the power factor and dielectric constant for a two-layer condenser

$$\tan \phi = kT/(1+k+\omega^2T^2) \tag{8}$$

$$K = K_0[1+k/(1+\omega^2T^2)] \tag{9}$$

where k and T are constants dependent upon the dielectric constants and the conductivities of the two media, and $\omega = 2\pi f$ where f is the frequency of the applied electromotive force.[2] It is evident that tan ϕ has a maximum value at the frequency for which $1+k=\omega^2T^2$. For frequencies so high that $1+k$ is negligible in comparison with ω^2T^2, tan ϕ will be inversely proportional to the frequency. The differences in behavior between actual dielectrics and the two-layer condenser he ascribes to the presence of more than two constituents. Since each impurity would produce a maximum power factor at a different frequency the effect upon the power-factor vs. frequency curve would be to make the maximum less sharp or even to produce several distinct maxima.

Since Pellat's theory that the electric displacement lags behind the field leads to a similar exponential equation for the reversible absorption current as a function of the time, whereas various observers had found the equation as experimentally determined to be of the form

$$i=\beta C_0 E t^{-n} \qquad 0<n<1 \tag{10}$$

where β and n are constants of the medium von Schweidler assumed a sufficient number of terms of the form of Eq. (7) to fit Eq. (10). Assuming in addition the principle of superposition enunciated by Hopkinson,[3] he derived the following expressions for the apparent capacitance and apparent conductance of a condenser when a sinusoidal electromotive force is applied.

$$C=C_0(1+A) \tag{11}$$

$$L=L_0+\omega C_0 B \tag{12}$$

where

$$A=\omega^{n-1}\beta\Gamma(1-n)\cos\left[(1-n)\pi/2\right] \tag{13}$$

$$B=\omega^{n-1}\beta\frac{\pi}{2\Gamma(n)\cos\left[(1-n)\pi/2\right]} \tag{14}$$

and C_0 and L_0 are the geometrical capacitance and the true conductance respectively.[4] The corresponding expression for the power loss is

$$P=E^2(L_0+\omega C_0 B) \tag{15}$$

If the loss due to conductivity is negligible, i.e., if $\omega C_0 B$ is large in comparison with L_0

$$P/E^2=\omega C_0 B=\text{const.}\, f^n \quad 0<n<1 \tag{16}$$

The derivation of Eq. (16) is independent of any theory as to the cause of absorption and merely states the law of variation of power loss with frequency to be expected if the absorption current obeys Eq. (10).

Sinjelnikoff and Walther, who have applied Joffé's theory that dielectric absorption is due to a counter electromotive force of polarization, to the alternating current phenomena, assume that for short intervals of time

[2] K. W. Wagner, Archiv. f. Elektrotech. **2**, 371 (1914).
[3] J. Hopkinson, Phil. Mag. **2**, 314 (1876).
[4] E. R. von Schweidler, Ann. d. Physik **24**, 711 (1907).

$$i = e^{-kt} \tag{17}$$

where $k = \sigma/c$, σ is the true conductivity and c the polarization capacitance. They derive the following expressions for the power factor and the power loss:

$$\tan \phi = \frac{\omega\sigma}{\bar{c}\omega^2 + \bar{c}k^2 + \sigma k} = \frac{\omega\sigma c^2}{\omega^2 c^2 \bar{c} + \sigma^2(c+\bar{c})} \tag{18}$$

$$P = E^2\omega^2\sigma/2(\omega^2 + k^2) = E^2\omega^2\sigma c^2/2(\omega^2 c^2 + \sigma^2) \tag{19}$$

where $\bar{c}$ is the geometric capacitance and E the applied potential.[5] The method of derivation is similar to von Schweidler's except that the exponential equation is assumed for the absorption current and that the constants are interpreted in terms of conductivity and polarization capacitance. Tan ϕ will have a maximum value where $\omega^2 = \sigma^2(c+\bar{c})/c^2\bar{c} \approx \sigma^2/c^2 = k^2$.

Assuming then that the power loss in dielectrics in alternating current circuits is due to absorption the finding of the law of variation of power factor or power loss with frequency should determine whether Eq. (7) or Eq. (10) correctly represents the absorption current, but not the cause of the absorption.

Since Eq. (2) which was found to fit the variation of power loss with frequency in the range from 800 to 4000 cycles is of the same form as Eq. (16) derived from von Schweidler's equations the n of Eq. (2) may be identified with the exponent of t in Eq. (10). This result confirms, for this range of frequencies, the conclusion of MacLeod.[6] Values of n obtained from the slope of the power loss curves, Fig. 1, are given in Table I, Column 2. These

TABLE I. *Values of n, β, K and K_0 for six samples of glass. The values of K have been corrected for edge effect by the method of Hoch[7] and hence are somewhat smaller than those given in Part I.*

Glass	n (from P/E^2)	n (from C)	β	K (1000 cycles)	K_0
1	0.84	0.89	0.034	7.25	6.77
2	0.89			4.79	
3	0.825	0.834	0.0077	6.54	6.46
4	0.82			4.56	
5	0.83			3.95	
6	0.83	0.86	0.0067	5.07	5.02

values are somewhat greater than the values of n, the exponent in Eq. (10) as experimentally determined by von Schweidler[4] and Tank[8] for various glasses, given in Table II. Race[9] finds the value of n for "PYREX" laboratory glass to be 0.62. The agreement between this value and 0.89 as determined from the power loss measurements, is not good.

[5] Sinjelnikoff and Walther, Zeits. f. Physik **40**, 786 (1927).
[6] H. J. MacLeod, Phys. Rev. **21**, 53 (1923).
[7] E. T. Hoch, Bell System Technical Journal **5**, 555 (1926).
[8] Franz Tank, Ann. d. Physik **48**, 307 (1915).
[9] H. H. Race, Paper presented before the A. I. E. E., New Haven, Conn., May 9–12, 1928.

TABLE II. *Values of β, n and power factor.*

Investigator	Dielectric	Method	β	n	Power factor
von Schweidler	Glass	Absorption	0.078	0.74	
"	"	"	0.0154	0.70	
Tank	Glass D	"	0.135	0.662	*0.0256
"	" E	"	0.115	0.697	*0.0218
"	" F	"	0.116	0.700	*0.0218
Race	‡"PYREX"	"		0.62	
MacLeod	Glass No. 2	Power Loss	0.037	0.86	†0.015
"	‡"PYREX"	"		0.885	
McDowell and	Glass No. 1	"	0.034	0.84	†0.011
Begeman	‡ " No. 2 ("PYREX")	"		0.89	†0.0082
"	" No. 4	"		0.82	†0.0039
"	" No. 6	"	0.0067	0.83	†0.0022
Granier	Glass	"		0.78	

* At 50.3 cycles.
† At 1000 cycles.
‡ The constants given for "PYREX" refer to the glass used for chemical ware. "PYREX" radio glass is No. 4.

As a further test of the applicability of the von Schweidler equations, n was calculated from the variation of capacitance with frequency. The writers are indebted to Dr. Chester Snow of the Bureau of Standards for the suggestion that if von Schweidler's constants A and B, Eqs. (13) and (14), be put into the form

$$A=\omega^{n-1}\beta\Gamma(1-n)\sin(n\pi/2) \tag{20}$$

$$B=\omega^{n-1}\beta\Gamma(1-n)\cos(n\pi/2) \tag{21}$$

Eq. (11) may be written in the form

$$C=C_0+(A/B)(BC_0) \tag{22}$$

or

$$C=C_0+(\tan n\pi/2)BC_0 \tag{23}$$

But from Eqs. (15) and (2), if $\omega C_0 B$ is large compared with L_0

$$BC_0\approx P/(E^2\omega)\approx C\tan\phi \tag{24}$$

Hence

$$C = C_0+\tan(n\pi/2)(C\tan\phi) \tag{25}$$

In Fig. 4 are shown values of C plotted as a function of $C\tan\phi$ for three of the glasses. The results appear to fit Eq. (25) as well as could be expected in view of the small magnitude of the change in capacitance with frequency. The total change in capacitance of glass No. 6 for a variation in frequency from 900 to 3500 cycles was less than $1\mu\mu f$ for a measured capacitance of about $300\mu\mu f$. Values of n obtained from the slope of these curves are given in Table I, Column 3. The agreement between the values of n obtained by the use of Eqs. (15) and (25), involving both the A and B of von Schweidler's Eqs. (13) and (14) appears to offer a fair test of the applicability of these equations to the power loss in glass within the frequency range considered. MacLeod by an equivalent method obtained for one glass corresponding values of n of 0.86 and 0.855.

Since the geometrical capacitance appears as the intercept of the line represented by Eq. (25) it becomes possible to calculate values of the true

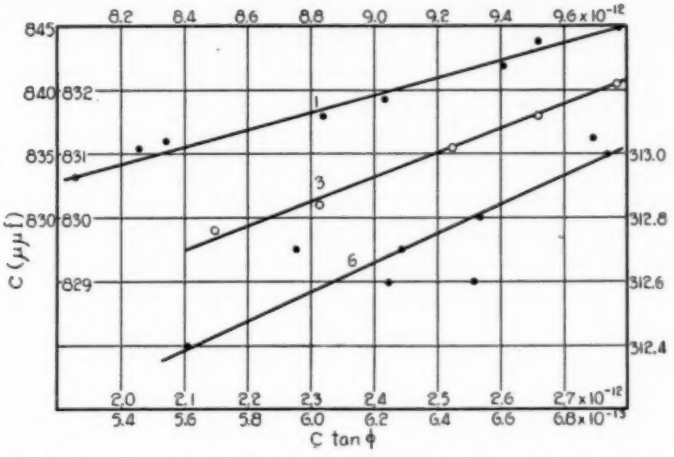

Fig. 4. Capacitance as a function of the product of the capacitance and the tangent of the phase difference for Glasses Nos. 1, 3, and 6. The coordinates are arranged from left to right and from top to bottom in the same order as the curves.

dielectric constant and of the constant β in the equation

$$i=\beta C_0 E t^{-n} \tag{10}$$

From Eqs. (24) and (21)

$$C \tan \phi = BC_0 = C_0(2\pi f)^{n-1}\beta\Gamma(1-n)\cos n\pi/2 = G/(f^{1-n}) \tag{26}$$

where

$$G = C_0\beta(2\pi)^{n-1}\Gamma(1-n)\cos n\pi/2 \tag{27}$$

Then

$$\log C \tan \phi = \log G - (1-n)\log f. \tag{28}$$

The intercept of the $\log C \tan \phi - \log f$ curves, Eqs. (4) and (28), gives the value of the constant G of which β is the only unknown factor.

In Table I, Column 5, are shown values of the dielectric constant as measured at 1000 cycles and in Column 6, values of the dielectric constant at infinite frequency calculated from Eq. (25). This use of Eq. (25) to obtain the value of the geometrical capacitance assumes that Eq. (10) holds for infinitely short intervals of time, an assumption which is almost certainly in error. Tank however found it to hold for intervals of time as short as 0.0003 second, Jordan for intervals of time between 0.13 second and 1.3 seconds.[9] Most investigators have measured the current only for times exceeding ten seconds and extending to hours or days. If the equation correctly represents the discharge current for times as short as 0.0003 second then the calculation of β by this method should lead to values in agreement with the experimentally determined values since the frequency range extended only to 4000 cycles. Values of β so calculated are shown in Table I, Column 4.

In Table II are shown values of the β and n of Eq. (10) as found by von Schweidler, Tank, and Race for various glasses and of n, the exponent in Eq. (2) as found by MacLeod, Granier[10] and the writers. Corresponding values of the power factor are given in the last column.

[10] J. B. Whitehead, Transactions A. I. E. E. **45**, 102 (1926).

The law of variation of power loss with frequency given by Eq. (2) probably does not hold for high radio frequencies. Measurements of the capacitance and series resistance of a condenser of Glass No. 1 were made by the resistance variation method[11] at frequencies from 100 to 1500 kilocycles. Up to frequencies of 100 or 200 kilocycles the von Schweidler equations appear to represent the variation of power loss and power factor with frequency fairly accurately. The values of n obtained from the slope of the log C tan ϕ − log f curve, Eq. (4) for frequencies between 100 and 200 kilocycles was 0.81 as compared with 0.84 for the audio frequency range. At frequencies above 200 kilocycles the capacitance continued to diminish with increasing frequency but the power factor passed through a minimum at a frequency of about 700 kilocycles and then rapidly increased. (See Fig. 5.)

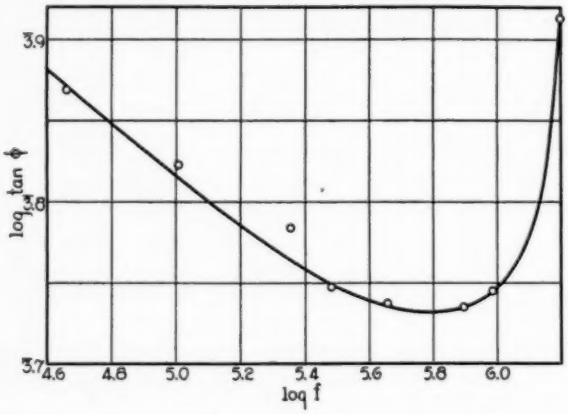

Fig. 5. The logarithm of the tangent of the phase difference as a function of the logarithm of the frequency, for Glass No. 1, at radio frequencies.

According to the Wagner theory this increase in the power factor indicates merely the presence of another impurity which produces a maximum value of the power factor at a much higher frequency, but the absence of other maxima through so wide a range of frequencies suggests the alternative possibility that a distinctly new cause of power loss is beginning to be effective at these higher frequencies. This increase of power factor with frequency at high frequencies is in partial agreement with the results obtained by Schott[12] who found the phase difference, ϕ, for several glasses to increase with increasing frequency between the frequencies of 200 and 600 kilocycles (1600 to 500 metres) although wherever comparison with low frequency measurements was possible the phase difference at a frequency of 2000 cycles or less was considerably greater than at the high frequencies. It contradicts the results of MacLeod[6] who found the power factor to diminish with frequency in accordance with Eq. (5) from 600 cycles to 1000 kilocycles.

To investigate the possibility that a maximum value of the power factor, as required by the equations of Sinjelnikoff and Walther, occurred at a

[11] Cir. No. 74, Bureau of Standards, p. 180.
[12] E. Schott, Jahrb. d. Draht. Tel. u Tel. **18**, 82 (1921).

frequency just below the range of frequencies measured, values of the power factor at two known frequencies were substituted in Eq. (18) and the equation solved for σ and $k=\sigma/c$. The results are shown in Table III. The

TABLE III. *Values of σ and $k=\sigma/c$*

Glass	$\omega_1/2\pi$	$\omega_2/2\pi$	tan ϕ_1	tan ϕ_2	$\sigma/\bar{c}$	σ	k	$k/2\pi$
1	851	2910	0.0116	0.00967	214	1.69×10^{-7}	8255	1301
	1445	2910	0.0108	0.00967	240	1.90×10^{-7}	10560	1680
2	830	1720	0.00757	0.00722	111	4.23×10^{-8}	6980	1111

complete lack of agreement with the experimental results is evident. The maximum value of the power factor should occur at a frequency $k/2\pi$, a frequency well within the range investigated where, as is evident from Fig. 2, there is no maximum. Furthermore the values of $\sigma/\bar{c}$ and k are not constant for the same glass, but differ according to the particular values of tan ϕ chosen for substitution in Eq. (18).

If the power loss is due to ionic conductivity, then the further possibility suggested itself of calculating the power loss directly from the apparent resistivity measured at a time equal to one-half the period of the applied electromotive force. Assuming that the measurements of resistivity of the various glasses as described in Part I were made approximately thirty seconds after the potential difference was applied, the power loss for a frequency equal to one-sixtieth of a cycle per second was found by extrapolation from the curves of Fig. 1 and the corresponding apparent parallel resistance of the condenser calculated from the relation

$$P/E^2=1/R_{ap}$$

The value so calculated was compared with the apparent resistance of the condenser calculated from the measured resistivity by the formula

$$R_{ap}=\rho d/A=K\rho/4\pi C$$

where K and C are respectively the dielectric constant and capacitance at 1000 cycles, in electrostatic units. The two values of the apparent resistance shown in Table IV are approximately of the same order of magnitude except

TABLE IV. *Apparent resistance R_{ap} calculated by two methods.*

Glass	1	2	3	4	5	6
R_{ap} from P/E^2 (ohms)	1.93×10^{11}	9.89×10^{11}	5.47×10^{11}	1.29×10^{12}	2.12×10^{13}	2.09×10^{13}
R_{ap} from ρ (ohms)	1.80×10^{10}	2.79×10^{11}	1.43×10^{12}	4.47×10^{13}	2.47×10^{13}	9.40×10^{16}

in the case of Glass No. 6, the glass of extremely high resistivity. For the borosilicate glasses without any heavy metals, Nos. 2, 4, and 5, the agreement is astonishingly good.

This agreement seems to be of sufficient significance to warrant further investigation and experiments are projected to measure the absorption current and the alternating current power loss at low frequencies for several glasses of varying properties.

The Effect of Temperature

The effect of change of temperature was studied in two ways: by finding the variation of power loss and power factor with frequency at several constant temperatures and by finding the variation with temperature at a constant frequency of 1000 cycles. It was found that Eqs. (2) and (3) still hold at the higher temperatures, but that n decreases with rising temperature. To determine whether the decrease in n is due solely to the fact that the conductivity increases rapidly as the temperature rises and that the power loss due to ordinary conductivity is independent of the frequency, there was subtracted from the total loss per second at each frequency the loss due to conductivity, $1/R_p$, determined by the formula $1/R_p = (1/\rho_t)(A/d) = 4\pi C/K\rho_t$, where K and C are respectively the dielectric constant and the capacitance at 1000 cycles, in electrostatic units, and ρ_t the measured resistivity at the temperature considered. Fig. 6 shows the logarithm of the corrected power loss plotted as a function of the logarithm of the frequency, for Glass No. 6, at three temperatures. From the slope of the power loss curves, both uncorrected and corrected for conductivity, values of n were computed for two glasses and are given in Table V.

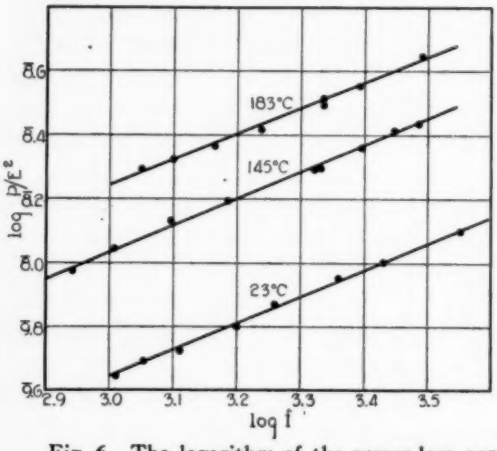

Fig. 6. The logarithm of the power loss per unit applied potential difference as a function of the logarithm of the frequency, for Glass No. 6, at three constant temperatures.

The results do not offer decisive evidence for or against any of the theories. The marked increase in power loss with temperature is in harmony

Table V. *Values of n.*

Glass	2	2	6	6	6
Temperature (degrees C)	25	95	23	145	183
Values of n					
Uncorrected	0.89	0.76	0.83	0.81	0.780
Corrected	0.89	0.84	0.83	0.81	0.785

with the conclusions of both von Schweidler[4] and Wagner[2] that the absorption current increases with rising temperature. The decrease in n is so slight as not to be widely at variance with the conclusion of von Schweidler that the rate of diminution of the absorption current with time is independent of temperature, i.e., that the n of Eq. (10) is not sensibly affected by temperature. According to Wagner the absorption current should decrease with time more rapidly at the higher temperatures.

Measurements of the power factor at the constant frequency of 1000 cycles were made between 30°C and 160°C. The values of tan ϕ corrected for conductivity, as shown in Fig. 7, fit the empirical equation

$$\tan \phi = Ae^{0.0077T} \tag{29}$$

where T is the absolute temperature. At liquid air temperature, the measured power factor was 0.0015 whereas if the same law holds it should be 0.00021. This apparent failure of the law at very low temperatures may be explained by the presence of strains produced in the glass by the rapid cooling. This explanation was borne out by the fact that measurements at four temperatures between −186°C and 0°C, made as the temperature was allowed to rise, indicated a power factor increasing steadily with the temperature and that the value of tan ϕ at room temperature, after immersion of the condenser in liquid air, was considerably higher than before, approaching more nearly the value for strained glass, reported in Part I.[1] According to the theory of Wagner the time constant, T, of Eq. (7) diminishes with increasing temperature and if the frequency be held constant there should be a maximum power factor at the temperature at which $1+k=\omega^2T^2$.[13] No maximum value was observed between −186°C and +160°C. The results are in fair agreement with the conclusion of Schott[12] that the increase of ϕ with increase of temperature is approximately exponential, but since the values of tan ϕ obtained by the writers were corrected for conductivity, Schott's explanation that the rapid increase is due to increasing conductivity, appears insufficient.

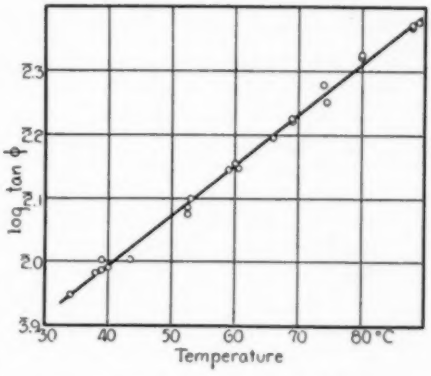

Fig. 7. The logarithm of the tangent the phase difference as a function of of temperature, for Glass No. 2.

Conclusion

The agreement with the equations of von Schweidler indicates that Eq. (10) correctly represents the absorption current for times as short as 0.0001 second and probably still shorter. As noted, this agreement is insufficient to determine the cause of dielectric absorption. The decision among the several theories must therefore rest, in part at least, upon other considerations than the variation of power loss and power factor with frequency and temperature.

The measurements recorded in Figs. 5 and 7 were made at the Bureau of Standards and the senior author gratefully acknowledges her indebtedness to Dr. H. L. Curtis and to Dr. J. H. Dellinger for placing the facilities of their laboratories at her disposal.

Wellesley College,
October 15, 1928.

[13] Die Isolierstoffe der Elektrotechnik ed. by H. Schering, 1–59 (1924).

A COMPARISON OF THE CORBINO AND HALL EFFECTS IN SILVER AND BRASS

By K. K. Smith and H. M. O'Bryan

Abstract

The method previously used by one of the writers to measure the Corbino effect by the electromagnetic torque on the circular disk has been improved. The torque is now balanced by sending a control current through one turn of insulated wire encircling the disk. The disk and control currents are led in and out through two pairs of spirals of silver ribbon. It is important to avoid magnetic impurities in the suspended system, and Navy Brass is found to be a thoroughly satisfactory material for the back disk. In fields of 8880 and 10100 gauss the Corbino coefficient, c, of silver is -5.9×10^{-7} and -5.8×10^{-7} e.m.u., respectively. Using a rectangular plate of silver and the method devised by Heaps, we find $c=-5.0\times10^{-7}$, the Hall coefficient $R=-8.6\times10^{-4}$ and the resistivity $\rho=1.72\times10^{3}$ e.m.u. These measured values agree well with those published in tables. For Navy Brass, the corresponding measured values are $c=-0.14\times10^{-7}$, $R=-0.96\times10^{-4}$, and $\rho=6.7\times10^{3}$ e.m.u. The difference between the values of c (for silver) obtained by the two methods used probably arises from differences in material in the circular disk and rectangular plate, respectively. The results now obtained by the improved method of measuring the torque indicate that the theoretical relation $c=R/\rho$ is satisfied. The discrepancies which appeared in the earlier experiments were doubtless produced by experimental errors, and by the change of resistivity of bismuth in the magnetic field.

Introduction

THE Corbino effect is produced when a circular disk of metal carrying a radial electric current is subjected to a magnetic field which has a component normal to the plane of the disk. Under these circumstances a steady circular current flows and its density varies inversely as the distance from the center. Corbino[1] demonstrated the existence of this small circular current by measuring the current which it induced in an adjacent coil when the radial current was made or broken. The effect is especially strong in a bismuth disk, and it has been found in a large number of other metals.[2] When the magnetic field, H, is normal to the plane of the disk, the total circular current is $C=cIH/2\pi \log (r_2/r_1)$, where I is the radial current, r_1 and r_2 are the internal and external radii, and c the Corbino coefficient of the metal.

The close connection between this new effect and the well known Hall effect was pointed out by Corbino[3] and by Adams,[4] who showed theoretically that the coefficients of the two effects are related very simply thus,

$$c=R/\rho, \tag{1}$$

[1] O. M. Corbino, Phys. Zeits., **12**, 561 (1911).
[2] E. P. Adams and A. K. Chapman, Phil. Mag., [6] **28**, 692 (1914).
[3] O. M. Corbino, Phys. Zeits., **12**, 842 (1911).
[4] E. P. Adams, Proc. Amer. Phil. Soc., **54**, No. 216, 47 (1915).

where R is the Hall coefficient, and ρ is the resistivity of the metal. Chapman[5] made a special experimental study of the relation between the two effects but found that Eq. (1) was not, in general, closely verified.

There is a second method of measuring the Corbino effect in a circular disk. When such a disk carrying a radial current is suspended in a magnetic field there is an electromagnetic torque acting upon it on account of the circular current which is itself produced by the magnetic field. Corbino[1] showed that this torque is

$$L = -cIH^2S_D \sin 2\phi/8\pi \tag{2}$$

where S_D is the effective area of the disk, and ϕ is the angle between the field and the normal to the plane of the disk. One of the present writers[6] tried this method and found that although the values of c deduced from measurements of the torques on disks of various metals were always of the same sign and order of magnitude as R/ρ, the values of c were in every case considerably less than R/ρ.

Using a *rectangular* plate through which he sent currents in mutually perpendicular directions, Heaps[7] was able to measure the Hall effect and the resistivity alternately; and since he had established Eq. (1) theoretically for his experiment, he used it to determine c. His results were in good agreement with other determinations of the three quantities in this equation.

Since the Corbino effect in its original form, i.e., in a circular disk, had not given results as satisfactory as might reasonably be expected, it seemed worth while to make a further study of the phenomenon in this form.

Purpose of the Experiments

The experiments to be described were undertaken in an attempt to measure as accurately as possible the torque which the magnetic field exerts upon the circular current. Silver was chosen as the material because its Hall coefficient and resistivity are well known and are independent of the strength of the magnetic field. A much larger effect might have been obtained by using bismuth, but at the same time, the values of R and ρ would have been more uncertain.

A second object was to compare the Corbino effect, thus measured, with the Hall effect in a rectangular plate cut from a sheet of silver. We have used, in the second part of the experiment, the method devised by Heaps because this gives information about both effects. Since the properties of the auxiliary brass which we used in the suspended system must be allowed for in a small correction term, we have also determined c and R for this material.

The Experimental Method

The first essential difference between the new and the old methods of measuring the Corbino torque is that the counterbalancing torque which

[5] A. K. Chapman, Phil. Mag., **32**, 303 (1916).
[6] K. K. Smith, Phys. Rev., **8**, 402 (1916).
[7] C. W. Heaps, Phys. Rev., **12**, 340 (1918).

holds the silver disk in the 45° position is now secured by the electromagnetic action on a control current which flows in a single turn of insulated wire encircling the disk. This control current can easily be varied until the torques are balanced. It is no longer necessary to touch the magnet or any part of the suspended system during the course of a determination. In the earlier experiments it was necessary to rotate the torsion head until the restoring couple of the twisted phosphor bronze suspension was sufficient to hold the disk in the 45° position. Apart from the greater slowness of the older method, it has the serious disadvantage that a rotation of the torsion head is almost certain to shift the center of the disk in one way or another. Although the magnetic field over the region occupied by the disk was sensibly uniform, it was a great improvement to avoid this displacement.

In the new method there is the additional advantage that the torsional coefficient of the suspension strip is not directly involved. This coefficient is likely to vary from day to day, because of temperature changes, etc., and cannot readily be redetermined without replacing the suspended disk by a body whose moment of inertia is known. The electromagnetic action depends, of course, only on the control current, the area which it encloses, and the field.

Another radical change in the apparatus was the replacement of tungsten needles dipping into mercury cups, by spirals of silver strip such as are used for lower suspensions in d'Arsonval galvanometers. The advantage of avoiding the "sticking" of the needles in a mercury surface which is hard to keep clean seemed to outweigh the disadvantage that the current carried by the spirals must be much less than that which a needle-mercury contact will carry. Attempts were made to use pieces of gold foil, or silver ribbon, in parallel, but without success.

Consider the system of disk and auxiliary parts suspended in a strong magnetic field which makes an angle of 45° with the normal to the plane of the disk. The torques acting upon the system are as follows: (i) A torque, N, produced by the elastic forces of the suspension wire and the spirals underneath. (ii) A torque, M, which depends upon the magnetic properties of the various materials in the field. Since this torque may vary slightly with the sense of the field produced by the electromagnet, let M_+ and M_- denote the values when this field is positive and negative, respectively. (iii) An Ampère torque which reverses when the field is reversed. This action, unfortunately, is very large, and seems to arise from the fact that the current flow is not strictly radial and symmetrical even in the absence of an external magnetic field. Let the Ampère torque be denoted by $a\,H\,I$, where a is a constant in the given position of the disk, and I, as before, the current sent through the disk. (iv) A Corbino torque, independent of the sense of H, which has its maximum value in the 45° position (cf. Eq. (2)) equal to $cIH^2S_D/8\pi$. (v) The control torque which has been varied until it exactly balances all the others, and the disk remains in the 45° position. If the control current is i, the torque is $iHS_c \sin 45°$, where S_c is the area enclosed by the single turn of wire.

Readings are taken with four combinations of H and I, as follows: (1) field *positive* and disk current *positive*; (2) field *positive* and disk current *negative*; (3) field *negative* and disk current *positive*; (4) field *negative* and disk current *negative*. Calling i_1, i_2, i_3, and i_4 the corresponding control currents, one can write the following equations of equilibrium for the suspended system.

$$N+M_{+}+aIH+cIH^2S_D/8\pi=-i_1HS_c\sin 45° \tag{3}$$

$$N+M_{+}-aIH-cIH^2S_D/8\pi=i_2HS_c\sin 45° \tag{4}$$

$$N+M_{-}-aIH+cIH^2S_D/8\pi=i_3HS_c\sin 45° \tag{5}$$

$$N+M_{-}+aIH-cIH^2S_D/8\pi=-i_4HS_c\sin 45° \tag{6}$$

Of the four unknown quantities N, M, a and c, the first three may be eliminated at once, and it is found that the Corbino coefficient has the following value

$$c=-\frac{2\pi S_c\sin 45°}{IHS_D}[(i_1+i_2)-(i_3+i_4)] \tag{7}$$

The signs in Eqs. (3), (4), (5) and (6) have been chosen in such a way that the mere magnitudes of the observed quantities H, I, i_1, i_2, etc., can be substituted, and the sign of c will be given correctly. A negative value of c (as in silver, for example) means that the circular current has the sense opposite to that of the magnetizing current when the radial current flows *in* toward the center.

Apparatus

The suspended system is shown in Fig. 1. In the first outfit the silver disk, D, was about 0.79 mm thick; its outer and inner radii were 10.5 mm and 0.5 mm, respectively. The material was fine silver supplied by Baker and Company, of Newark, New Jersey. This was soldered into a brass collar, A, about 4 mm long. The right end of this collar was threaded on the inside so that it could be screwed tightly to a back disk, B, of brass. This disk was divided into octants by radial saw cuts in order to prevent a circular current from flowing. The back disk was silver soldered to a bent brass tube, T, 4.3 mm. in diameter outside.

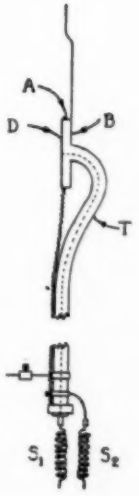

Fig. 1. Diagram of suspended system

Inside the tube an insulated wire carried current to the center of the silver disk. This current flowed into the wire through the silver spiral S_1; after passing through both disks and the tube it flowed out through the spiral S_2. The end of the tube was about 17 cm below the center of the disk.

The control current flowed in a single turn of D.S.C. copper wire, B. & S. No. 32, which encircled the collar tightly. The remainder of the wire, shown as a zig-zag line in the figure, formed an adynamic pair of leads which were joined near the bottom of the tube to two vertical spirals *not* shown in the figure.

A stiff brass wire which was soldered to the back disk carried a plane mirror, and the whole outfit was supported by a fine phosphor bronze ribbon about 55 cm long. A counterpoise attached to the lower part of the tube enabled us to shift the center of gravity until the center of the tube at the lower end was directly under the center of the disk.

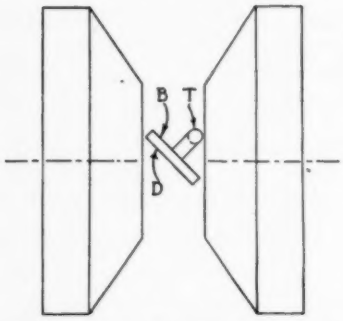

Fig. 2. Plan of suspended system between poles of electromagnet.

Fig. 2 shows the plan of the apparatus, suspended between the poles of a Weiss electromagnet. For most of the experiments the gap was 21 mm long (nearly equal to the diameter of the disk). The pole faces were 50 mm in diameter. The entire suspended system was enclosed in a box with glass windows.

Since the Corbino torque varies as the square of the magnetic field, it was important to keep the field as constant as possible. The magnetizing current, usually about 34 amp., was sent through a manganin resistance and by means of a potentiometer this current was kept very constant while observations were being made. The windings of the Weiss electromagnet were copper tubes and the water circulation was adjusted to keep the electromagnet at room temperature. The field, H, was measured, on reversal, with a Grassot fluxmeter and a Société Genevoise search coil whose effective area was accurately known. Exploration of the region occupied by the disk showed that the field was sensibly homogeneous.

A telescope and scale were used to determine when the disk was in the 45° position. The observer who kept the magnetizing current constant also adjusted the control current by sliding resistances until he found that the disk remained in equilibrium in the desired position. Then the other observer, who had been using a Leeds and Northrup Type K potentiometer to measure the control current immediately made a final balance and thus determined the proper value of i.

The current I was set at a definite value, usually about 0.300 amp., at the beginning of an experiment, and although it remained constant for long periods of time its value was always checked closely before and after the other observations were made.

Results of Experiments on Circular Disks

In the first outfit the collar, back disk and tube were made from commercial brass. The wire to the center of the silver disk was stranded copper wire covered with rubber. Ordinary soft solder was used in the connections to the silver disk, and to the brass tube. A large amount of time was spent in attempting to get reproducible results. Over 60 determinations gave an average value $c = -7 \times 10^{-7}$ e.m.u. But it seemed likely from the variations in successive values of the control currents that the magnetic im-

purities in the brass, solder, rubber, etc., were vitiating the results. The magnetic torque, on the average, was about sixty times the Corbino torque which we were trying to measure. The Ampère torque was about one hundred times the Corbino torque, but this fact was not so troublesome because the Ampère effect is at any rate constant.

A second outfit was therefore constructed, and precautions were taken to avoid materials containing magnetic impurities. The front disk and the collar were in one piece, turned out of a block of c.p. silver from Baker & Company. Hard silver solder was used to fasten a silver wire to the center of the disk. "Spaghetti" insulation, instead of rubber was used between this wire and the tube. The brass tube was discarded, and replaced by a silver one. From the Naval Research Laboratory we obtained, through the kindness of Dr. W. H. Crew, a rod of "Navy Brass" which is practically free from magnetic impurities. And like other varieties of brass it has a very small Corbino coefficient, and is therefore thoroughly satisfactory for use in the back disk. By taking special precautions in the construction of all the parts and cleaning them in hydrochloric acid, the magnetic torque was reduced to one-eighth of its value in the first disk. We were surprised, however, to find that the results yielded a very small but *positive* Corbino coefficient. We dismantled the outfit, but could not find any flaw in construction or short circuit in the connections. As soon as the third outfit was tried, we discovered that the apparent value of c increased over 100 percent when a second determination was made after the ammeter for measuring I had been turned 180°. The mean of the two values was not far from the mean of a large number of later determinations in which a *potentiometer* was used to measure the disk current. It seems probable that in the case of the second outfit where we used the ammeter to make the few measurements that we obtained, the error due to a stray field from the electromagnet had led us to use slightly more current for one direction of H than for the other. Since in the second outfit the Ampère torque was about 300 times as great as the Corbino torque, the error might easily have overbalanced the effect which we were trying to measure.

The third outfit was practically a duplicate of the second, except that the *back* disk of Navy Brass was not divided by radial saw cuts. Hence it was necessary to apply a slight correction for the Corbino effect in the brass disk. This was done by subtracting from the effective area of the silver disk a small fraction of the area of the brass disk. This small fraction was the ratio of the Corbino coefficient in brass to that in silver. Independent experiments, to be described later, had shown us that $c=-0.14\times10^{-7}$ e.m.u. for the brass, and we assumed the approximate value $c=-5.9\times10^{-7}$ e.m.u. for the silver. This correction amounted to 0.079 cm². A still smaller correction was made for the *silver* in the cross section of the tube. One half of this area was 0.017 cm² and this amount was subtracted from the area of the front disk.

The outside diameter of the collar was 2.225 cm; the inside diameter was 1.93 cm. Taking account of the two corrections just mentioned, and using the mean diameter of the collar, one has

$$S_D=(\pi/4)(2.077)^2-0.079-0.017=3.292 \text{ cm}^2.$$

The area of the control turn was $S_c=3.906$ cm².

The first four determinations of c made while using a potentiometer to measure I are shown in Table I. Each value of the control current, i, is the mean of two readings and is expressed in milliamps.

TABLE I. *Results obtained with circular disk.*

		$I=0.30403$ amp.		$H=8880$	
i_1	i_2	i_3	i_4	$(i_1+i_2)-(i_3+i_4)$	c
17.087	15.499	15.366	16.923	0.297	-5.80×10^{-7}
17.085	15.506	15.372	16.918	0.300	-5.86
17.092	15.524	15.698	16.583	0.335	-6.54
17.098	15.474	15.361	16.936	0.275	-5.37

Later measurements showed smaller variations, and after rotating the electromagnet (which carried the torsion head, housing, etc.) through 180°, and replacing a broken suspension, we obtained the values shown in Table II.

TABLE II. *Further results obtained with circular disk.*

		$I=0.30403$ amp.		$H=8880$	
i_1	i_2	i_3	i_4	$(i_1+i_2)-(i_3+i_4)$	c
17.624	16.076	15.924	17.465	0.311	-6.08×10^{-7}
17.556	16.005	15.870	17.388	0.303	-5.93
17.544	15.993	15.844	17.386	0.307	-6.00

The average of 13 determinations, including those shown in Tables I and II, is $c=-5.93\times10^{-7}$ e.m.u.

Then the magnetic field was increased to 10,100 gauss and 8 determinations were made. The average value of c is -5.83×10^{-7} e.m.u. Giving equal weight to each of the 21 values which we obtained, we find that $c=-5.88\times10^{-7}$ e.m.u.

EXPERIMENTS ON RECTANGULAR PLATES

In order to check the preceding determinations of the Corbino effect, we have used Heap's method[7] on rectangular plates of silver and Navy Brass. Details of the way in which a plate is prepared are given in his paper, and it seems unnecessary to repeat them here, since our procedure was essentially the same as his.

Let the face of the plate be taken as the XY plane and let a and b be the effective dimensions parallel to the X and Y axes, respectively. Let the magnetic field H act parallel to the Z axis and let the thickness of the plate be t. A sensitive galvanometer is connected to the middle points of those sides of the rectangle which are parallel to the Y axis.

Now if a current I_y flows in the plate while the field is acting, the Hall effect will be proportional to the galvanometer deflection produced by reversing the field. Let D' be one-half of this deflection. Then,

$$R=D'st/I_yH, \tag{8}$$

where s is the voltage sensitivity of the galvanometer circuit.

The current I_y is now interrupted and a small current I_x is sent at right angles to the former current. The resistivity is then given by Ohm's law, as follows:

$$\rho = D''sbt/aI_x \tag{9}$$

where D'' is one-half the galvanometer deflection observed on reversal of I_x. Therefore, dividing one equation by the other, we have

$$c = \frac{R}{\rho} = \left(\frac{a}{b}\right)\cdot\left(\frac{I_x}{I_y}\right)\cdot\left(\frac{D'}{D''}\right)\cdot\left(\frac{1}{H}\right) \tag{10}$$

Eqs. (8), (9) and (10) are the laboratory equations for calculating R, ρ, and c from the observations. It should be noted, however, that this method by itself gives no independent check on the validity of the relation $c = R/\rho$; the correctness of the values calculated from the laboratory equations can be tested only by comparison with the results of other experiments. We have found the values shown in Tables III and IV. These give for brass

$$\rho = \frac{R}{c} = \frac{-9.6\times10^{-5}}{-1.43\times10^{-8}} = 6.7\times10^{3} \text{ e.m.u.},$$

which agrees as well as could be expected with the value, 6.6×10^{3}, given in Kaye and Laby's Tables. So far as we know the Corbino coefficient for brass has not previously been measured. Hall[8] found $R = -12\times10^{-5}$ for brass (Cu 67 percent, Zn 33 percent).

TABLE III. *Results obtained with rectangular plate.*

				Navy Brass				
$a = 1.55$ cm				$b = 1.20$ cm				$t = .039$ cm
H	I_y amps	D′ cm	I_x amp	D'' cm	D'/D''	s microvolts per cm	R	c
9140	5	0.15	0.02	6.47	0.022	0.654		
		0.18		6.46	0.028	0.654	-9.7×10^{-5}	-1.41×10^{-8}
		0.18		6.60	0.028	0.653		
		0.18		6.65	0.026	0.642		
16400		0.30		6.62	0.046	0.638	-9.6×10^{-5}	-1.45×10^{-8}
						average	-9.6×10^{-5}	-1.43×10^{-8}

Our measured values for silver agree as well as could be expected with those published in tables. Thus the average of the four values of R (for silver at room temperature) given in Campbell's *Galvanomagnetic and Thermomagnetic Effects*, p. 124, is -8.45×10^{-4} e.m.u. Chapman[5] gives four values of c; the average is -4.88×10^{-7} e.m.u. And according to Kaye and Laby's Tables, ρ (at 18°C) is 1.66 or 1.63×10^{3}.

CONCLUSIONS

The torque method gives a direct and trustworthy measure of the Corbino effect, although the difficulties of measuring this minute effect are great

[8] E. H. Hall, Phil. Mag., **19**, 261 (1886).

TABLE IV. *Results obtained with rectangular plate.*

Silver: $a=3.0$ cm; $b=3.0$ cm; $t=0.079$ cm

H	I_y amps	D' cm	I_z amps	D'' cm	s microvolts per cm	D'/D''	R	c	ρ
16400	5.0	1.31	0.10	3.34	0.666	0.392			
		1.33		3.29	0.674	0.404			
		1.31		3.28	0.668	0.400			
		1.34		3.27	0.668	0.409			
	7.5	2.06	0.15	4.90	0.665	0.420			
		2.10		4.87	0.672	0.431			
					average	0.411	-8.67×10^{-4}	-5.01×10^{-7}	1.73×10^{3}
9380	7.5	1.15	0.15	4.91	0.664	0.234			
		1.13		4.88	0.658	0.232			
	5.	0.75	0.10	3.27	0.678	0.229			
	7.5	1.13	0.15	4.86	0.679	0.233			
	5.	0.75	0.10	3.23	0.668	0.232			
	10.	1.50	0.20	6.46	0.677	0.232			
	5.	0.75	0.10	3.24	0.680	0.231			
					average	0.232	-8.51×10^{-4}	-4.95×10^{-7}	1.72×10^{3}
16580	7.5	2.00	0.15	4.83	0.680	0.414			
		1.99		4.78	0.678	0.416			
	10.	2.63	0.20	6.38	0.683	0.412			
		2.64		6.40	0.678	0.413			
					average	0.414	-8.59×10^{-4}	-5.00	1.72×10^{3}
					average		-8.6×10^{-4}	-5.0×10^{-7}	1.72×10^{3}

when the magnetic and Ampère torques are superposed upon it. The value of c obtained for silver by this method is -5.9×10^{-7} whereas a smaller value, -5.0×10^{-7} e.m.u., was found when measures were made on a rectangular plate by Heaps' method. It seems reasonable that the differences in the material in the two cases might account for the difference between the two measured values of c.

In regard to the criterion, $c=R/\rho$, it must be remembered that the disk and collar were turned out of a small block, and we have no measurements of its resistivity. The earlier results[6] obtained by one of the writers were undoubtedly affected by large experimental errors, especially in the case of the metals in which the Corbino effect is small. The apparent discrepancy between c and R/ρ for bismuth is largely accounted for by the increase of ρ in the magnetic field. Considering all the experiments that have now been made by the torque method, we see no reason for doubting that the relation $c=R/\rho$ is the correct one.

We wish to express our appreciation of the assistance of Mr. A. Krause, who constructed most of the parts for the suspended system.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILLINOIS.
Sept. 21, 1928.

THE EFFECT OF CORONA CURRENT ON THE COOLING OF A HOT WIRE*

By Samuel R. Parsons

Abstract

This article describes an experimental study of the cooling of a hot wire in air, when the air is disturbed by a corona discharge to the wire. With a copper wire, No. 30 B. & S. gauge, *in still air*, no effect was found with corona current less than 3 microamperes per cm of wire; but beginning with about that value, the cooling power of the wire increases, at first rapidly, and then more slowly, possibly passing through a poorly defined maximum. A corona current as great as 12 microamperes per cm is sufficient to give nearly the maximum effect. With small currents of air past the wire, a gradual increase of corona current, starting with zero, often shows first a heating effect, followed by a cooling effect. The slow currents of air seem to be appreciably retarded by the cross-flow of the ions carrying the corona current. The number of ions required for appreciable cooling is estimated to be considerably less than one ion per million molecules of the gas.

A SMALL wire gently heated in still air dissipates heat rather slowly, because of the fact that the air close to it forms an effective heat-insulating blanket; and any agency that disturbs this insulating blanket may be expected to increase the loss of heat from the wire. It has seemed probable that if the electrical potential of a wire is raised until a corona discharge is obtained, the motion of the ions in the corona current should cause an appreciable cooling effect. This has been found to be true, and the cooling power of a wire has been doubled, with rather small corona current. The following paragraphs describe an experimental study of this cooling effect.

Perhaps it should be stated that since the experiments are subject to the irregularities of cooling with very feeble convection currents, and also to the irregularities of the corona discharge, too much significance must not be attached to the absolute magnitudes of quantities shown. The results of the experiments should be regarded as representative of similar, but not identical, values that might be obtained under very slightly different conditions.

Apparatus

A piece of No. 30 bare copper wire, 17.2 cm long, was stretched along the axis of a brass tube of the same length, and 4.3 cm inside diameter. This wire, which will be called the "corona wire", was supported at both ends by current and potential leads of No. 22 enameled copper wire. The ends of the brass tube, supported by insulating rings of Bakelite panel-

* Research Paper No. 105, Journal Series, University of Arkansas.

board of 10.5 cm outside diameter, opened directly into wooden boxes about 15 cm square and 6 cm deep. In the side of each box opposite the opening of the brass tube was a hole 4.5 cm in diameter, covered with glass. The glass windows allowed direct observation of the corona wire, and by means of small holes drilled at their centers, additional wires were used to help center the corona wire, and to provide means for applying a suitable tension. The boxes were made fairly tight except for a 0.5 inch hole drilled in one side of each. Aside from acting as supports, they provide air chambers allowing some ventilation of the tube while shielding the corona discharge from air currents in the room. In a corona tube with closed ends, it has been found that with a steadily applied voltage, the corona current changes in value after a few seconds, perhaps largely because of the rise in temperature and the formation of ozone; but by the use of these boxes, very steady values of corona current were obtained, so long as the axis of the tube was horizontal. Its use in a vertical position was not satisfactory.

Alternating current was used for the corona discharge, the high potentials being obtained from a 25,000 volt, 1 k.v.a. transformer. The corona current passing between the wire and the tube was measured by means of a Western Electric vacuum thermocouple and sensitive galvanometer.

The corona wire was heated by direct current from a storage battery, and a standard current carrying resistance was placed in series with it. Potential drops across the corona wire and the standard resistance were measured by a potentiometer method,[1] furnishing data from which to compute the current in the wire, its resistance, and the rate of development of heat in it, or its rate of dissipation of heat. The temperature coefficient of resistance of the wire was found from direct measurements on a piece cut from the same spool, and the wire was used to measure its own temperature. It was not feasible to measure the temperature of the air in the corona tube by this method, because when the current was small enough to avoid heating the wire, the readings on the potentiometer were too small to be reliable. The resistance of the wire without heating current was accordingly measured by the use of a Mueller thermometer bridge with special commutator—the method used with four-lead resistance thermometers, whereby the resistance of the leads is entirely eliminated. The temperature of the wire obtained from this measurement was assumed to be equal to the temperature of the air surrounding it.

The high potential circuit was grounded close to the corona wire, and so arranged that the corona tube was the only part at high potential, so that measurements could be made in the heating circuit without interference from the 60–cycle corona current.

No attempt was made to dry the air, and at times the relative humidity was as high as 85 percent.

[1] The instrument used was the "millivolter" of the Pyrolectric Instrument Co., with an auxiliary galvanometer.

Results

The cooling due to corona current is shown most directly in Fig. 1, which shows the lowering of temperature of the wire, under a certain constant heating current, as the corona current is increased. (Wherever temperature is represented in the figures, it will be shown by the difference in temperature between the wire and the air in the corona tube.) But since the resistance of the wire changes as its temperature changes, a constant heating current does not insure a steady rate of production of heat, and the cooling power of the wire is better shown in Fig. 3, where the rate of dissipation of heat is shown as a function of the corona current, for constant differences of temperature between the wire and the air. The direct results of experiment are represented by curves of which those of Fig. 2 are typical, and Fig. 3 is made from values read from these curves. Fig. 4 shows similar values obtained for the same corona wire and tube, but about a year later.

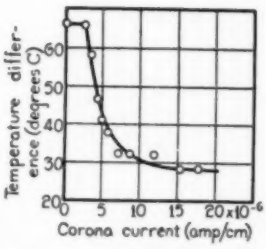

Fig. 1. Cooling of wire by corona current. "Temperature difference" is difference in temperature between the wire and the air surrounding it.

The curves show that a minimum corona current of about 3 microamperes per cm of corona wire is necessary to cause sufficient disturbance of the air for appreciable cooling; and that as the corona current increases, the cooling power of the wire increases rapidly at first and then more slowly, apparently reaching a maximum value. Very little further cooling is obtained by raising the corona current above 12 microamperes per cm. If the rate of dissipation of heat really passes through a maximum, as some of the curves seem to indicate, it is probably due to local heating of the air close to the wire, by the corona current itself; for a corona current of 25 microamperes per cm required a potential difference of 8 kilovolts, representing 0.2 watt per cm.

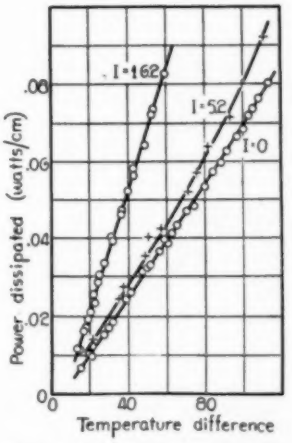

Fig. 2. Rates of dissipation of heat with corona current. *I* is the corona current in microamp. per cm of wire.

The corona current required for appreciable cooling was also found by another method: with a certain heating current flowing, the potentiometer was balanced on the potential drop across the corona wire, and the corona current was gradually increased until the potentiometer was thrown out of balance. This was also done with low rates of flow air through thy corona tube. The results are shown in Fig. 5. An interesting secondars effect was observed when air was flowing through the tube: in many casee, when the corona current reached about the value necessary for appreciable cooling in still air, the potentiometer was thrown out of balance in the

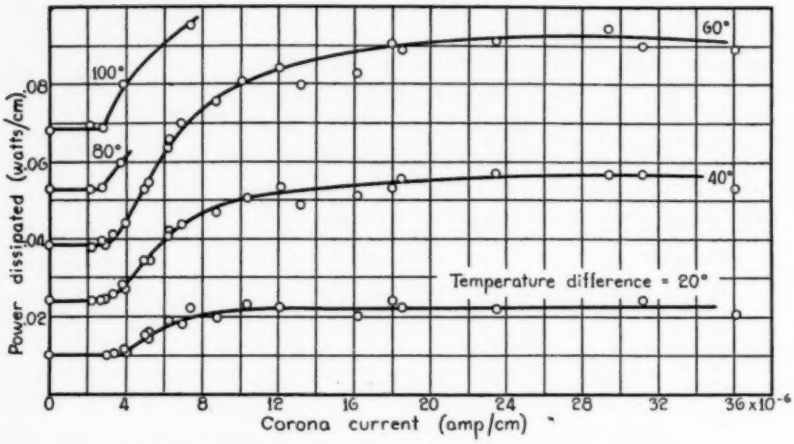

Fig. 3. Effect of corona current on cooling power of wire.

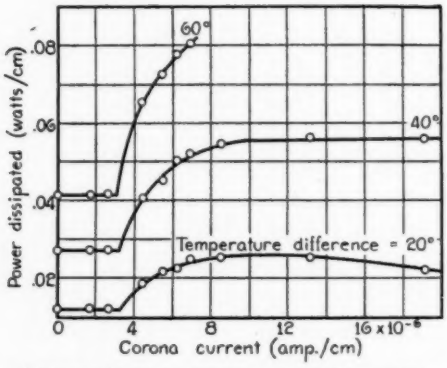

Fig. 4. Effect of corona current on cooling power of wire.

direction indicating *heating* of the wire, and some further increase of corona current was required to show a cooling effect. It is as if with low rates of flow, a small corona current interferes with the air stream close to the wire enough to reduce its cooling effect, while a larger corona current causes enough disturbance of the air to add to the cooling effect of the stream. With a higher rate of flow and a small heating current, the corona current gave a heating effect for the largest value used, which was 11 microamperes per cm. Fig. 6 is included to show the order of magnitude of the effects of air flow on cooling power of the wire, without corona current.

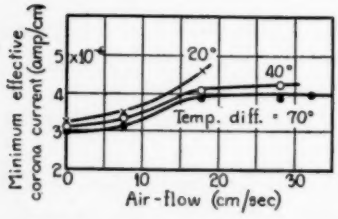

Fig. 5. Effect of flow of air on minimum corona current required for appreciable cooling.

With a given potential difference across the corona tube, the application of the heating current was found to cause some increase in the corona current. This is probably due to the rise in temperature of the air, which is known to result in greater corona current.[2]

[2] Fazel and Parsons, Phys. Rev., 23, 598 (1924).

An attempt was made to obtain similar data with a second corona wire, No. 36 gauge, but so much trouble was caused by vibration of this fine wire that no satisfactory data could be obtained. No vibration was detected with the corona current alone, but with fairly large corona current, and a heating current of about 2 amperes, the vibration of the wire was so violent that it set up a hum much louder than the hum of the transformer.

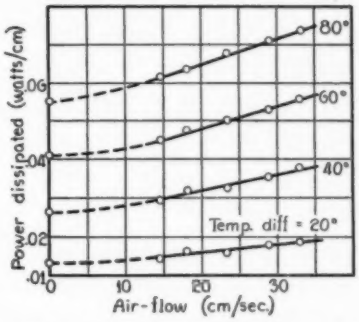

Fig. 6. Effect of flow of air on cooling power of the corona wire, without corona current.

Estimated Space Charge

It is interesting to estimate the number of ions per cubic centimeter that are required to show a cooling effect. In the corona tube, most of the ionization is confined to a region close to the wire, while the remainder of the tube contains (during a half-cycle) ions of only one sign. The density of this space charge is readily computed, on the basis of two or three assumptions. Let i be the current per cm length of wire and tube; ρ, the density of space charge; and u, the velocity of the ions at any distance r from the axis of the wire. Then the current per cm passing a cylindrical surface of radius r is

$$i = 2\pi r \rho u \tag{1}$$

If we assume that the velocity of the ions is proportional to the field, we may write $u = kX$, where k is the mobility of the ions; and X, the intensity of electric field. If the current is small, the electric field is nearly that of the electrostatic case, namely,

$$X = V/r \log_e (R/r_0) \tag{2}$$

where V is the potential difference between wire and tube; R, the radius of the tube; and r_0, the radius of the wire. From these equations,

$$i = 2\pi \rho k V/\log_e (R/r_0) \quad \text{or} \quad \rho = i \log_e (R/r_0)/2\pi k V \tag{3}$$

The disappearance of the factor r shows that the space charge is uniform throughout the space considered—outside of the region of intense ionization.

Unfortunately, this equation involves the mobility of the ions, about which rather little is known. If we should assume that the initial ions are like those formed by x-rays or radioactive substances, it would be safe, for the purpose of this estimate, to call the mobility 1.8 cm/sec per volt/cm; for the life of the ions is so short that very few of the positive ions have the time for the "ageing" observed by Erikson and by Wahlin.[3] But by measurements on ions taken from a corona tube, Young[4] has found mobilities very

[3] H. A. Erikson, Phys. Rev., **20**, 117 (1922); H. B. Wahlin, Phys. Rev., **20**, 267 (1922).
[4] W. M. Young, Phys. Rev., **28**, 129 (1926).

much lower than this, and distributed over a wide range of values. His values for oxygen range from 0.92 to 1.8×10^{-4} cm/sec per volt/cm; and his values for nitrogen lie within this range. His measurements were made on ions more than 2.5 seconds old.

The table shows the space charges computed by means of Eq. (3), using the three values of mobility indicated. The number of molecules

TABLE I. *Space charge accompanying lowest corona current that shows a cooling effect.*

Assumed mobility, cm/sec per volt/cm	1.8	0.92	0.00018
Space charge, e.s.u. per cm^3	2.0	4.0	2.0 (10^4)
Number ions per cm^3	4.2 (10^9)	8.3 (10^9)	4.3 (10^{13})
Ions per molecule	1.8 (10^{-10})	3.5 (10^{-10})	1.8 (10^{-6})

present in one cubic centimeter of gas at the pressure and temperature existing in the corona tube (about 25°C, 72 cm) is about 2.4×10^{19}, and the last line of the table is obtained by dividing the number of ions per cubic centimeter by this number. If each ion consisted of one molecule, this would be the fraction of the number of molecules of the gas that must be ionized before appreciable cooling results; but if the ions have mobilities as low as were found by Young, they must be much greater than one molecule, and the figures in the last line of the table represent merely the number of ions per molecule of the gas. The average numbers of ions per cubic centimeter so close to the wire as to be within the region of intense ionization, would be somewhat less than twice the values shown in the table, since the space charge outside of that region represents all the ions of one sign formed. (The conditions are such that recombination of ions is negligible.)

Since, according to Young, the mobilities are distributed in unknown proportions over a wide range of values, no close estimate can be made of the conditions in the corona tube, but is seems safe to state that less—probably very much less—than one ion per million molecules is sufficient to disturb the air close to the wire enough to cause an appreciable change in its cooling power.

THE UNIVERSITY OF ARKANSAS,
September 11, 1928.

AN EXPERIMENTAL STUDY OF THE GROWTH OF ZINC CRYSTALS BY THE CZOCHRALSKI-GOMPERZ METHOD

By A. G. Hoyem and E. P. T. Tyndall

Abstract

The conditions necessary to grow zinc single crystals of 2.7 mm diameter and of any desired orientation are determined experimentally. When a constant rate of growth is used and the crystal is initially given the desired orientation by starting it on a suitable nucleus the determining factor for the successful growth of a single crystal rod 10 cm or more in length is found to be the temperature gradient existing in the column of liquid zinc just below the growing crystal. The appropriate temperature gradient is a function of the orientation of the crystal. It is depicted graphically in a figure which shows the upper and lower limiting curves for the region of successful growth when the rate of growth is 1.2 cm/min. The lower curve rises from orientation 0 to 45° and falls from 45 to 90°. The upper curve lies slightly above and parallel to the lower curve from 0 to 50°, but then rises very sharply. The shape of this region does not seem such as to be attributed only to variation in heat conductivity with orientation. Attempts to grow crystals outside of the appropriate region result in sudden or gradual changes to new orientations. In the latter the orientation shifts gradually through a considerable range. Illustrations are given of such changes.

Introduction

ALTHOUGH several investigators have used the Czochralski[1]-Gomperz[2] method for the production of single-crystal rods of zinc, the conditions necessary to obtain a rod of any definite diameter and desired orientation[3] seem to have been largely empirical and suited to the particular form of the apparatus used. The variables on which the diameter of the rod and its orientation must depend are: (1) temperature of the molten zinc; (2) rate at which the crystal is grown; (3) the method used to cool the portion of the crystal already grown; (4) starting conditions, i.e., whether the crystal is started on a nuclear crystal or on a foreign body, such as a glass or copper rod.

Gomperz[2] employed a rate of growth of from 12 to 6 mm per min., and kept the molten zinc at from 25 to 30° above the melting point, in order to obtain ductile (dehnbar) single crystal wires. With the temperature 3° to 5° above the melting point and a corresponding rate of 30 to 60 mm per min., he obtained brittle single crystal wires. The diameters of the crystals ranged from 0.1 to 1.5 mm. They were all started on a glass rod. A stream of N_2 was passed through the apparatus to prevent oxidation of the molten zinc. It undoubtedly also produced a cooling effect, though not a definitely controlled one. He makes no mention of the orientations of the crystals

[1] Czochralski, Zeits. f. phys. Chem., **92**, 219 (1917–18).

[2] Gomperz, Zeits. f. Physik, **8**, 184 (1922).

[3] The term orientation is used to define the angle between the vertical axis of the crystal and the axis of the rod.

grown, but it may be assumed that the ductile crystals had orientations between 20 and 70°, while the brittle crystals were either nearly 0 or else nearly 90°, since ductility and brittleness generally characterize these particular types of single crystals.

Mark, Polanyi, and Schmid[4] grew ductile crystals using a "high temperature" (not stated specifically) and a rate of 12 to 6 mm per min. Under these circumstances, however, only fifty percent of the trials resulted in successful crystals. They found further that the impurity of the zinc must be less than 0.03 percent to grow these ductile crystals. Using a rate of less than 6 mm per min., they found that brittle crystals could always be grown, signifying by brittle crystals those having an orientation of 90°. They employed a blast of gas directed at the portion of the crystal already grown, for the specific purpose of cooling it. The crystals were started on a foreign body apparently.

Grüneisen and Goens[5] were apparently the first to use a crystal fragment as a nucleus on which to start the new crystal. Their experience of the conditions of growth was at variance with that of others. They were very successful in growing crystals of various orientations and assumed that the blast of cooling gas was an important factor. They stated, further, that with a very slow rate they obtained crystals of 0° (or nearly 0°) orientation, but noted that if the rate was too fast, the crystal would change to approximately 90°.

The Czochralski-Gomperz method was first used in this laboratory by E. G. Linder[6] to grow zinc crystals. Later[7] the apparatus was improved, and a certain empirical procedure was worked out to produce crystals of desired orientations. At first the crystals were started on copper wires and later on nuclear crystals. The method as developed by Linder was, however, still largely a matter of trial and error, and he was not able to produce with certainty a crystal rod of a particular diameter and any specified orientation. During the earlier work, he produced some crystals the orientation of which varied continuously along the lengths of the rods. He states[6] that such crystals were grown at an "excessive rate" (probably more than 10 mm a minute), but no further specifications are given. The air blast which he used was directed towards the surface of the zinc in the crucible and was not used specifically to cool the solid crystal rod.

A mica disk, floating on the surface of the molten zinc and pierced with a circular hole through which the crystal is drawn, has been used by almost all observers and was used throughout in the work described below.

In the fall of 1927, one of the present writers (E.P.T.T.) attempted to place the growth of zinc crystals by this method on a less empirical basis. Linder's second apparatus was used with some slight modifications, which have in the main been adhered to in the work and which will be described

[4] Mark, Polanyi, Schmid, Zeits. f. Physik, **12**, 58 (1923).
[5] Grüneisen and Goens, Zeits. f. Physik, **26**, 235 (1924).
[6] E. G. Linder, Phys. Rev. **26**, 486 (1925).
[7] Linder, Phys. Rev., **29**, 554 (1927).

below. It was concluded that (1) the rate of growth was not a determining factor in the production of a given orientation; (2) for a given diameter of crystal and given (constant) rate of growth, a crystal of any orientation might be grown if it was started on a nucleus of the desired orientation and was grown with a temperature of the molten zinc appropriate for that orientation; (3) the temperature gradient existing in the column of liquid zinc just below the solidified crystal (see Fig. 1(a)) is the main factor under-

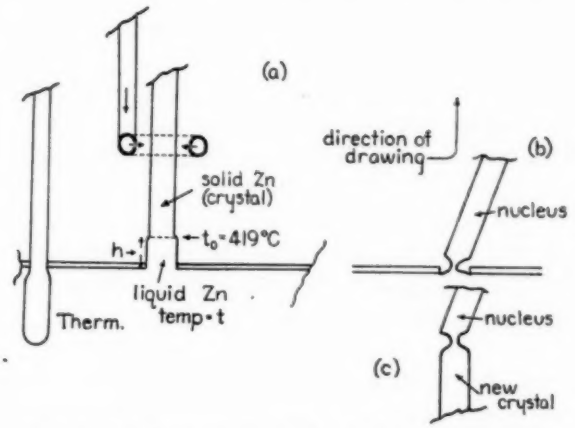

Fig. 1. To illustrate method of growing zinc crystals.

lying the continued growth of a particular orientation which has been started on a nucleus. This work has been described briefly elsewhere[8] and will not be further elaborated on, as the present paper covers the same ground more fully and is in substantial agreement with the earlier work.

The main object of the present investigation was to obtain more particularly and exactly the relation between this temperature-gradient and the orientation, and, if possible, to shed light on the general problem of the process of crystallization from the liquid state.

Apparatus

A description of the apparatus has been given by Linder.[9] The tube used for a blast of air by Linder was not so used in this investigation, but a special form of "ring nozzle," placed about 15 mm above the surface of the molten zinc, directed streams of air radially at the crystal. This is shown in detail in Fig. 1(a). A thermometer and a thermocouple were also placed in the molten zinc, the latter being directly below the hole in the mica, through which the crystal is being grown. (It is not shown in the figure.) A stream of CO_2 is admitted through a glass tube (not shown in figure) to keep the surface of the melt free from oxide prior to and during the insertion of the nucleus. No gas passes through this tube during growth of the crystal.

[8] E. P. T. Tyndall, Phys. Rev., **31**, 313 (1928).
[9] Ref. 7. Fig. 1.

Procedure

The procedure which is used in growing a single crystal rod having a definite diameter and orientation is essentially as follows. A portion of a crystal having the desired orientation is inserted in the drawing apparatus with its length parallel to the direction of drawing or, if a crystal nucleus having the desired orientation is not available, a portion of a crystal of somewhat different orientation is inserted in the holder in such a way that its principal axis makes the desired angle with the direction of drawing. This situation is depicted in Fig. 1(b) and (c). The mica disk previously referred to is now pushed up on the nuclear crystal, so that this nucleus passes through the circular hole in the center of the disk. The diameter of this hole is just about equal to the desired crystal diameter. The zinc in the crucible is then heated until it attains a temperature approximately 50° above the melting point (419°C). A small stream of CO_2 is then passed through the tube previously mentioned. The space above the surface of the molten zinc is thus freed of air. The film of oxide which has previously formed on the surface is skimmed off by means of a glass rod, and the lower end of the nucleus is pushed below the clean surface of the melt. The mica disk is then dropped down and floats on the surface. The stream of CO_2 is now stopped. Fig. 1(b) represents this stage of the process, a well defined "neck," having formed at the junction of the molten zinc and the nucleus. The "ring nozzle" is then adjusted around the nucleus, and the air turned on rather strongly so that the cooling of the molten zinc to the desired temperature of growth is accelerated. When the temperature has become steady at a value within the temperature range in which the crystal is to be grown, the air is adjusted to the right value and the drawing mechanism is started. During the growth of the crystal the temperature is kept as constant as possible. The air blast may be adjusted slightly from time to time, if necessary, in order to keep the crystal diameter equal to that of the hole in the mica disk. A record is kept of the temperature at the start and, as nearly as possible, of every change of temperature, together with the corresponding length of the crystal at the time that the temperature change takes place. It is found that a greater degree of success is attained if the nucleus has the same diameter as the crystal to be grown, since this eliminates the possibility of oxide forming between the mica and the crystal. If such oxide is present, it may adhere to the sides of the crystal and thereby serve as a new nucleus on which another crystal may start. The need of having the surface of the molten zinc entirely free from oxide at the time when the nucleus is inserted can also not be too highly stressed.

The Growth Process

After the crystal has been growing several minutes, it is in the condition shown in Fig. 1(a). The temperature of the liquid zinc just below the hole in the mica is t. Above this point there is a small cylindrical column of liquid zinc the top of which is at temperature t_0 (=419°C, the melting point of the zinc). There is probably little lateral loss of heat in this column; thus

the temperature gradient is axial (i.e., parallel to the axis of the rod, not crystal axis), and may be considered as proportional to $(t-t_0)$, provided the height, h, of the liquid column is the same for all crystals. It is further assumed that this height is the same for crystals of the *same* diameter being drawn at the *same* rate. The function of the air blast is twofold: (1) to cool the crystal far enough above the plane of solidification so that the heat flow may be normal to this plane, (2) to fix the size of the crystal. Thus, the larger the diameter of crystal for a given temperature of melt, or the higher the temperature for a given diameter, the stronger must be the blast of air.

The conclusion of one of the writers, previously stated, that the determining factor underlying the growth of a particular orientation is the temperature gradient in the liquid column, is of course based on the assumption of proportionality between this temperature gradient and the temperature difference $(t-t_0)$.

In order to obtain the range of this temperature gradient in which a crystal having a definite orientation and diameter should grow, an attempt is made to grow crystals at every few degrees of temperature above the melting point until a temperature is found at which a crystal 10 to 18 cm in length can be obtained. Having found this temperature, the process is continued until both the highest and the lowest temperature at which the crystal can be grown are known. In a similar manner the range for other orientations is obtained, the rate of drawing being kept constant for all orientations.

Materials

Two lots of Reagent Zinc Merck were used in obtaining the data herewith presented. The analyses given on the containers differ slightly. The first lot has as maximum limits of impurities 0.000025 percent of arsenic, 0.0056 percent of matter oxidizable by permanganate (as Fe), and 0.0000 percent of compounds of sulphur and phosphorus. The second, which was used in the latter part of the experiments, contains as maximum limits of impurities 0.000025 percent of arsenic, 0.028 percent of matter oxidizable by permanganate (as Fe), and 0.0020 percent of chlorides. The latter grade proved somewhat easier to handle since it is only slightly subject to oxidization when exposed to air, even at a temperature of 60° above the melting point.

Results and Discussion

Fig. 2 is a graphical representation of the results which have been obtained for crystals 2.7 mm in diameter drawn at a rate of 1.2 cm per minute. The circles indicate successful crystals grown and are restricted to those which have the same orientation throughout and which are at least 10 cm in length. The crosses signify crystals which were unsuccessful, that is, crystals which grew 1 cm or more with the orientation with which they were started but then changed either gradually or suddenly to a different orientation, the change not being caused by oxide or any other imperfection on the crystal surface or in its interior. The mean of the temperature during

the growing of the crystal is used in plotting the successful crystals, while in the case of the unsuccessful ones the approximate temperature at which the change in orientation took place is plotted. The two smooth curves, drawn so as to lie in the region of uncertainty, therefore represent the extreme limits of temperature at which a crystal can be grown. Hence the region between them is the temperature range in which the particular orientations will grow. Crosses lying far exterior to the limits are not plotted in order that the graph might be clearer; this refers especially to the region of high temperature for crystals below 50° orientation.

The 90° (or nearly 90°) crystals are seldom found to change. They are very readily grown and can be obtained in a very wide range of temperature, which seems evident from the rapid rise of the upper limit curve from 60°

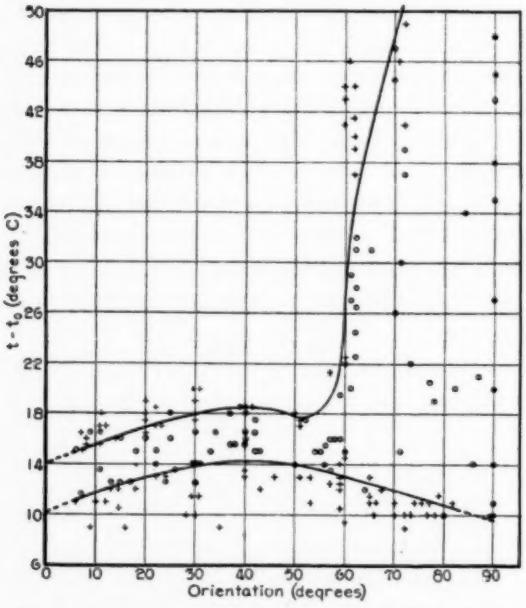

Fig. 2. Graphical representation of the results obtained in growing zinc crystals.

to 70°. No attempt was made to grow 80° or 90° crystals with temperatures above the upper limit for the 70° crystals, because the extreme amount of cooling which is necessary at these high temperatures could not be conveniently produced. The lower limits for the 0° (or nearly 0°) and the 90° crystals were not obtained with any degree of definiteness on account of the nearness of approach to the solidification point of the zinc.

It is to be noted that the crosses and circles overlap slightly. This is due to the fact that successful crystals can occasionally be obtained in the region of uncertainty, provided that the temperature remains very constant, while unsuccessful ones are of course also obtained there. It may be noted here that there are no crosses at 30° orientation higher than $(t-t_0)=11.5°$, and it may be that there is a depression in the lower limit curve in this neighbor-

hood. The writers, however, do not believe this very probable and have not drawn the curve to include this possibility.

Four points which might have been plotted as crosses have been omitted. They are definitely cases of crystals which changed orientation when well within the region in which they should grow. One of these cases was apparently due to the apparatus running somewhat jerkily; a second is of particular interest since it is that of a 90° crystal changing to 73°, the only case of such a change that the writers have ever observed or heard of. There is no obvious explanation for this change, nor for the other two cases.

As already mentioned, crystals started within the appropriate range of temperature and grown at or beyond either limit of this range change orientation either suddenly or gradually. A sudden change in orientation is characterized by a new crystal, which has an orientation different from the original, starting abruptly within the crystal rod without there being any flaw within or on the surface of the rod to which the change might be attributed. These sudden changes occur (1) for the second lot of zinc, when the temperature goes several degrees beyond (i.e., above or below) the limits of the region of successful growth and remains there fairly constant, (2) for the first lot of zinc, as soon as the temperature passes the limits. In these cases of sudden change, the new orientation is usually higher (in 77 cases out of 80 observed) than the original, and the new crystal always crowds out the old after the rod has grown a few centimeters as a double crystal. Temperatures several degrees beyond either limit seem to accelerate this crowding. It is found further that crystals of orientations between 6 and 40°, in changing suddenly, seldom change to crystals having orientations less than 60°. If, however, such a crystal does change to an orientation lower than 60°, a second sudden change usually occurs, giving a final orientation above 70°.

When a crystal changes orientation gradually, the orientation changes continuously along the length of the rod without any evidence of a new crystal entering. Crystals showing this gradual change were, almost without exception, obtained only with the second lot of zinc. A gradual change is caused: (1) by starting a crystal within the range and going below the lower limit, in which case a low orientation (6 to 30°) crystal will shift to a slightly higher one, and a high orientation (50 to 85°) crystal to a lower one; (2) by starting within the range and exceeding the *upper* limit, in which case both the low orientations (6 to 25°) and the high orientations (60 to 70°) shift to slightly higher orientations; (3) by starting and growing the crystal just exterior to the limiting temperatures. It is found difficult, in going below the lower limit, to cause a high orientation crystal (50 to 85°) to shift to below 40°. Usually, if a crystal shifts from 70° down to about 45°, it will change suddenly to a higher orientation if the temperature is kept fairly constant below the range.

Fig. 3 shows the behavior of some of these variable orientation crystals. The "limit" curves are superimposed on the graph in order that the variations in temperature and orientation may be more easily understood. In the lower part of the figure is plotted orientation against temperature above

the melting point. Directly above is a graph showing the relation between the orientation and length for each crystal represented. Consider for example curve (a), Fig. 3. A 75° crystal starts at 13° above the melting point,which is well within the range, and the temperature falls until it is 11° above, at which point the orientation begins to shift. By following the arrows on the curve, one sees that the orientation remains constant at the beginning and end of the crystal, when the temperature is within the range, but varies when it is exterior to it. Curve (a′), Fig. 3, shows the relation between the length and orientation for this same crystal. Cases of this kind could be produced at will. In curve (b), Fig. 3, is shown a case in which the orientation begins to shift as soon as the temperature begins to fall. A sudden shift to a higher orientation occurs when the orientation has reached 52°. Had the temperature been increased to within the range at this point (similar to the procedure followed in curve (a)) the crystal would undoubtedly have continued to grow with this orientation. Several such instances of a gradual

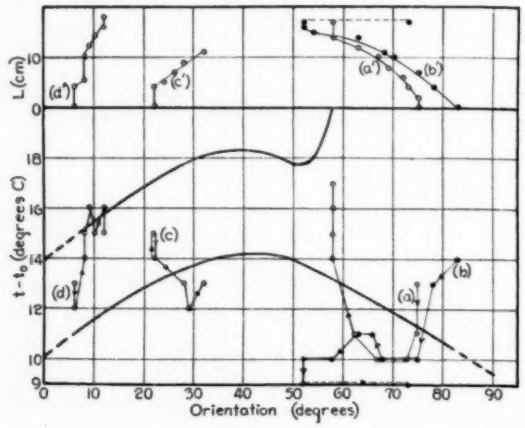

Fig. 3. Showing the behavior of some of crystals of variable orientation.

change followed by a sudden change have been noted, the sudden change always being to a higher orientation. This second change is concordant with the type of sudden change previously discussed. Curves (c), (c′), (d) and (d′) illustrate typical shifts for low orientation crystals.

Besides the variable orientation crystals just discussed, the following peculiar crystals were obtained which are of interest: (1) A 31° crystal which grew uniformly and was straight when the temperature remained within the range, but became slightly crooked and rough when the temperature exceeded the upper limit; perhaps in so doing it was able to retain its original orientation. (2) A 52° crystal which changed suddenly to an orientation of 77° and then this second crystal after a few centimeters of growth changed suddenly to a 65° crystal. This is the only "secondary" sudden change to a lower orientation which has been noted. (3) A 53° crystal which changed suddenly to another 53° crystal when the temperature was below the lower limit. The temperature then entered the range and the crystal continued to grow with

the second 53° orientation. The two 53° crystals were so situated in the rod that the axis of the rod and the two vertical crystal axes were in the same plane, that is, the two crystal axes made the largest possible angle with each other.

After the experimental results presented above had been obtained, an effort was made to determine what effect a change in rate of growing the crystals would have on the limit curves. The new rate used was 2.2 cm per minute. Fifteen crystals were grown, the majority of which had orientations of approximately 50°. The results seem to indicate that the lower limit curve for the 50° orientation crystals is raised considerably higher. No definite statement, however, can be made as to the remaining part of the curve. Interesting gradual changes were observed. Two crystals, 82° and 80° orientation, started at a temperature near the lower limit curve for the 1.2 cm per minute rate, were made to shift gradually to orientations of 49° and 44°, respectively, during a crystal length of 15 cm. These shifts are considerably greater than any observed at the rate of 1.2 cm per minute. It is inferred that this is due to two causes: (1) the temperature of growth is probably well below the lower limit for the 2.2 cm per minute rate; (2) the higher rate accelerates the shifting. The explanation for the crystals grown by Linder[6] with orientations varying from approximately 90° to 45° is thus apparent.

Conclusion

The most important result is believed to be the substantiation of the fact that the temperature gradient existing in the liquid zinc just before it solidifies is the main factor determining the continued and successful growth of a particular orientation. Thus there is no particular "crystallization velocity" associated with a certain orientation. The writers do not mean to imply that, for a particular orientation, the permissible value, or range of values, of this gradient is independent of the velocity of growth. Were this so, the region included in the limiting curves of Fig. 2 would always be the region of successful growth, regardless of the velocity of growth.

For crystals of different orientation, but of the same diameter and grown at the same rate, the most obvious factor which varies with the orientation is the thermal conductivity of the crystal. Since, however, the reciprocal of this quantity is a linear function of the square of the cosine of the angle of orientation and thus has no maximum or minimum between 0° and 90°, it is difficult to see how the region of successful growth shown in Fig. 2 can be predicted from considerations of crystal conductivity alone. It seems more likely that the determining gradient in the liquid (or in the solid), in addition to depending on the crystal conductivity, is also an independent function of the orientation.

University of Iowa,
Iowa City, Iowa,
October, 1928.

THE TUBE-CORRECTION IN MEASUREMENTS OF THE VELOCITY OF SOUND IN GASES

By R. E. Cornish and E. D. Eastman

Abstract

The evidence concerning the validity of the Helmholtz-Kirchhoff equation $\Delta V/V_0=[\eta^{1/2}+(\kappa/c_v)^{1/2}(\gamma-1)/\gamma^{1/2}]/D(\pi\nu d)^{1/2}$ for the change in velocity of sound in a tube, in terms of the viscosity, thermal conductivity of the gas, diameter of tube and frequency of the sound, including some tests by existing data not hitherto utilized for this purpose, is summarized and discussed in this paper. The indications are that the equation is correct, within the limits of error, at the higher frequencies and larger tube-diameters usually employed in present day measurements. Under such conditions, this method of correction appears to be the most reliable available. A convenient approximate expression is deduced for the variation of the correction with temperature, and the constants required for its application calculated for several gases. At low frequencies and for small tubes, as commonly employed in the older measurements, the adequacy of the Helmholtz-Kirchhoff equation is not established. Partly for this reason and partly because they may correct other errors, the methods of correction that depend upon the inverse diameter law are to be preferred under these conditions, and perhaps in all cases where enough precision of measurement is obtainable. On the other hand, the system of tube-calibration by measurements with a standard gas, especially as applied in much recent work at high temperatures, is in practice particularly subject to large errors, and is theoretically justified only if the Helmholtz-Kirchhoff equation is correct.

TO ACCOUNT quantitatively for the reduction in the speed of propagation of sound, due to the effect of viscosity and conduction of heat at the surface of containing tubes, Kirchhoff,[1] amplifying the earlier work of Helmholtz,[2] deduced an equation which, for small decrements, may be written as follows:

$$(V_0-V)/V_0=\Delta V/V_0=[(\eta)^{1/2}+(\kappa/c_v)^{1/2}(\gamma-1)/(\gamma)^{1/2}]/D(\pi\nu d)^{1/2} \qquad (1)$$

In this equation V_0 is the velocity in the free gas, V the measured velocity in the tube, η is the viscosity, κ the thermal conductivity, d the density and c_v the specific heat of the gas at constant volume, and γ is the ratio of its specific heats at constant pressure and constant volume. The diameter of the (cylindrical) tube is represented by D and the frequency of the sinusoidal oscillation by ν. It is assumed in the derivation that the layer of gas in contact with the tube adheres to it, and that the walls of the tube are rigid and remain at constant temperature, i.e., that they are of very great heat capacity or conductivity as compared with the gas.

Numerous experimental investigations of the validity of Eq. (1) have been made. Many conflicting results have been obtained and divergent conclusions drawn, with consequent confusion and distrust of the theory.

[1] Kirchhoff, Ann. d. Physik **134**, 177 (1868).
[2] Helmholtz, Crelles Journal **57**, 1 (1859).

It is the purpose of this paper to discuss the present status of the equation, introducing some new tests by existing data, and urging considerations not hitherto given sufficient weight. The possibility of its application at high temperatures, where it becomes of much importance in connection with the determination of specific heats of gases, is the particular object toward which this work is directed.

In nearly all of the earlier investigations[3] bearing upon Eq. (1), the dust figure method of Kundt was employed. It is obvious theoretically and found experimentally that the presence of dust in the tube further diminishes the velocity of sound in it. While the effect of the dust may be minimized by favorable choice of amount and fineness, it must always constitute a doubtful factor. Results by this method can be given little weight, and conclusions based on them can scarcely be carried over to the more modern methods.

Schulze,[4] however, employed the resonance method of Quincke. Working with very small tubes and at relatively low frequencies (the most severe conditions of test), he found the calculated correction too small and observed that the velocity was different in tubes of the same diameter but of different materials. The order of the variation of the correction in relation to the material of the tube can certainly be predicted from the thermal properties (heat capacity per cubic centimeter and conductivity for heat). Schulze's results, however, are not systematically related to these quantities, a fact that casts doubt on their validity and indicates the presence of some spurious effect. The more recent and more precise results of Dixon, Campbell and Parker[5] with larger tubes of lead, steel and silica glass showed no detectable dependence of the velocity upon the material of the tube.

Stevens,[6] also employing a resonance method, was able to obtain very consistent values of V_0 by a method of calculation depending upon combination of measured velocities in various pairs of tubes of differing diameters. He considered that his results substantiated the Helmholtz-Kirchhoff theory. In fact, however, his calculations prove only that the correction is very closely inversely proportional to D, which is an obvious necessity by any theory. To see to what extent his results are in agreement with Eq. (1), the corrections corresponding to his conditions have been calculated by it. The values corrected by the equation are shown in column 6 of Table I, together with the corrected values found by Stevens (last column). The agreement is by no means perfect. It is best, however, in the experiments of greatest accuracy (Nos. 1 and 2). Moreover, it will be observed that while the corrections calculated from Eq. (1) for the experiment at 20° are smaller than found by Stevens' method of combination, at 100° they are larger. These facts suggest that the method of combination (or

[3] Kundt, Ann. d. Physik **135**, 337, 537 (1868); Schneebelli, ibid, **136**, 296 (1869); Seebeck, ibid, **139**, 104 (1870); Kayser, ibid, **2**, 218 (1877); Low, ibid, **52**, 664 (1894); Müller, ibid, **11**, 331 (1903); Stürm, ibid, **14**, 822 (1904).

[4] Schulze, Ann. d. Physik **13**, 1065 (1904).

[5] Dixon, Campbell and Parker, Proc. Roy. Soc. London (A), **100**, 1 (1921).

[6] Stevens, Ann. d. Physik **7**, 285 (1902); Verh. deut. phys. Ges. **3**, 54 (1901).

extrapolation), corrects not only for the genuine effect of the tube upon the velocity of sound, but for certain minor apparent effects due to imperfections in the method or technique of measurement.

TABLE I. *Tube corrections to the velocity of sound in air from measurements of Stevens.*

No.	Material of tube	Diameter of tube mm	Temp. °C	Measured Velocity meters/sec.	V_0 calc. meters/sec.	V_0 comb. meters/sec.
1	Porcelain	40.4	20	341.19	342.73	343.27 (40–20)
2	Porcelain	29.5	20	340.47	342.57	343.15 (40–30)
3	Porcelain	20.2	20	339.11	342.18	—
4	Chamotte	46	20	340.80	342.15	343.25 (46–23)
5	Chamotte	23	20	338.36	341.04	—
6	Porcelain	40.4	99.6	385.51	387.66	386.90 (40–20)
7	Porcelain	29.5	99.6	384.95	387.89	387.03 (40–30)
8	Porcelain	20.2	99.6	384.12	388.42	—

Recent studies by Grüneisen and Merkel[7] and Cornish and Eastman[8] confirm the Helmholtz-Kirchhoff equation. Their work was done with hydrogen and with air in tubes ranging from 2.5 to 10 cm in diameter and at frequencies ranging from 5000 to 12000 cycles per second. The average of their results with hydrogen at 0° as computed by the inverse diameter law agrees within the limit of error with that calculated by Eq. (1). The latter equation applied to the results of Cornish and Eastman with air at 24° gave entirely consistent values of V_0 with two tubes of different diameters. The results of Grüneisen and Merkel with air at 0° are also in close agreement with the Helmholtz-Kirchhoff equation. Contrary to most of the earlier results, the correction is larger in the instance calculated by them from the equation than obtained by extrapolation.

Most of the experiments cited in the preceding were at temperatures not far removed from atmospheric. For the desired application to specific heat measurements, the variation of the correction at high temperatures must be known. Partly for the purpose of carrying out such tests of the equation as can be made at high temperatures, and partly with the view of supplying a convenient form of the equation for use in the elevated range, some consideration has been given to this question.

For convenience in discussion, the quantities in Eq. (1) that are properties of the gas may be gathered together into a single factor, C, the equation then being written

$$\Delta V/V_0 = C/D(\pi\nu)^{1/2} \tag{2}$$

in which

$$C = [(\eta)^{1/2} + (\kappa/c_v)^{1/2}(\gamma-1)/(\gamma)^{1/2}]/(d)^{1/2} \tag{3}$$

It is now desired to obtain C as a function of the measured quantities V and T (absolute temperature). The error allowable in the correction depends, of

[7] Grüneisen and Merkel, Ann. d. Physik **66**, 344 (1921).

[8] Cornish, and Eastman, J. Am. Chem. Soc. **50**, 627 (1928). (Eq. 22, p. 646 of this reference was incorrectly transcribed. Values in Table IX were calculated, however, from the correct equation.)

course, upon the accuracy desired in the results for the derived specific heats. If the latter is set at 1 percent, it will usually prove sufficient to know C within 10 percent. This limit enables the use of equations involving γ, d, V and T based on the behavior of ideal gases, but applicable with enough exactness in most of the real cases of interest. We may thus make use at once of the equations

$$d = pM/RT \tag{4}$$

and

$$\gamma = MV^2/RT \tag{5}$$

in which p is the pressure and M the molecular weight of the gas. For the remaining quantities of Eq. (3) (viscosity and thermal conductivity), use will be made of certain results of the kinetic theory.

It has been shown by Chapman[9] that in any gas whose molecules follow an inverse power law of force, the viscosity is expressible by an equation of the form

$$\eta = kT^n \tag{6}$$

where k and n are constants characteristic of the gas. The degree to which this behavior is followed by a number of representative gases is shown in Figure 1. In this figure, the logarithm of the measured viscosities[10] is plotted against the logarithm of the temperature. The linear character of the curves so obtained justifies the use of equations of the form of (6) for interpolation and extrapolation. From the curves, values of the constants have been calculated and are tabulated below.

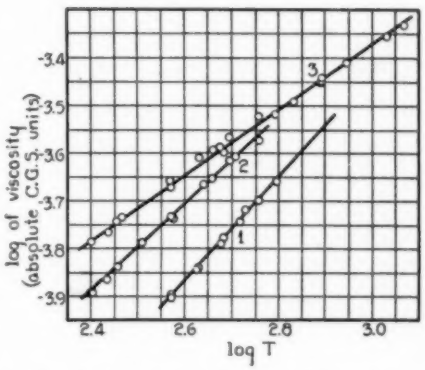

Fig. 1. Viscosity of gases. Curve 1, H_2O; curve 2, CO_2; curve 3, air.

TABLE II. *Constants of Equation (6) connecting viscosity (in absolute C.G.S. units) and temperature of gases.*

Gas	N_2	Air	H_2O	CO_2
k	2.28×10^{-6}	3.48×10^{-6}	2.04×10^{-7}	8.67×10^{-7}
n	0.765	0.696	1.085	0.905

The thermal conductivity is known from kinetic theory to be related to the viscosity, and to γ. Jeans,[11] combining the theory of Chapman with a suggestion of Eucken obtains the semi-theoretical result,

$$\kappa = \tfrac{1}{4}(9\gamma - 5)\eta c_v \tag{7}$$

and shows it to be well substantiated experimentally. An equation of a different form, wholly empirical and equally well verified experimentally

[9] Chapman, Phil. Trans. A, **216**, 279 (1916).

[10] From Landolt-Börnstein, Tabellen, which may be consulted for detailed references.

[11] Jeans, Dynamical Theory of Gases, Cambridge Univ. Press, p. 318 (1916).

has been proposed by Pollock.[12] This equation proves slightly less convenient than the one above in the present connection and for that reason has not been employed. The agreement as applied to individual cases, of the two very different equations may, however, be regarded as an indication of the correctness of the values obtained by them.

The combination of Eqs. 3, 4, 5, 6, and 7 leads finally to the expression, (writing a for M/R),

$$[C=(k/ap)^{1/2}T^{(n+1)/2}1+1.12(1.8-T/aV^2)^{1/2}(aV^2/T-1)] \qquad (8)$$

Eq. (8) is approximately valid at all temperatures and pressures at which the gas concerned does not deviate greatly from the ideal. For comparison, values calculated by it are given in Table III below, together with some calculated by Dixon, Campbell and Parker[5] and by Shilling.[13] These authors employed the Sutherland formula for the extrapolation of viscosity somewhat after the manner of Fürstenau.[14] The differences are larger in some instances than the desirable limit of error. It is believed that those calculated by Eq. (8) are to be preferred to the others.

TABLE III. *Values of constant C of Equation 2.*

Gas	Temp. °C	C (Eq. 8)	C, Dixon	C, Shilling
CO_2	600	0.998	0.97	1.017
CO_2	1000	1.31	—	1.398
N_2	1000	2.03	1.85	—
H_2O	1000	1.95	—	1.643

For the testing of Eq. (8) at high temperatures, only a few rather inaccurate data[15] by Stevens relating to air at temperatures between 850 and 1000°C are available. These results, obtained with tubes of 40 and 20 mm diameter, are plotted in Figure 2. The determinations with the smaller tube are represented here by circles and those with the larger by crosses. The latter are less consistent than the former, and allow much latitude in the placement of a curve to fit them. The curve drawn by Stevens (Ref. 6a, p. 306) can scarcely be right since it deviates less at the higher temperatures from the measurements with the small tube than it does at lower. To make the test desired here, therefore, the procedure was as follows. The best curve (Line 1, Fig. 2) for the smaller tube was assumed to be correct. Employing Eq. (8) the speeds that should have been found in the larger tube, if the equation is correct, were calculated. These are given by Line 2 of Figure 2. This line falls somewhat outside the region included by the four measured points,

[12] Pollock, J. Roy Soc., New South Wales, **49**, 249 (1915); Phil. Mag. **31**, (1916).

[13] Shilling, Phil. Mag. **3**, 273 (1927).

[14] Fürstenau, Ann. d. Physik **27**, 735 (1908).

[15] The first experiments of Stevens (Ref. 6, a) at high temperatures which are the ones used here, were made under very difficult conditions. The experiments were later repeated (Ref. 6, b) with better facilities and greatly improved accuracy, but the detailed results were not published.

indicating that the theoretical correction is too small. The theoretical curve, however, does not differ from the line best fitting the experimental points much more than the poorer points deviate from it. If it be assumed that minor defects of method (such as the failure of exactly integral ratios between the quarter and half wavelengths, mentioned by Stevens), were not of equal influence in the two sets, the discrepancy may be further reduced. While the disagreement appears, therefore, greater than the error, and perhaps points to partial failure of the equation at low frequencies, the intimation persists that this is not the case in view of the good results by the more accurate methods at low temperatures, and the reversal in sign of the discrepancy in Stevens' own work at 100°. It at least emphasizes the necessity of further study in this field. It should be noted at this point that Stevens' own method of treating his results is considered entirely justifiable and right, provided that the improved accuracy in his final work (Ref. 6, b) permitted definite placement of his curves. From the general high quality of the other portions of his work, this may be assumed to have been the case.

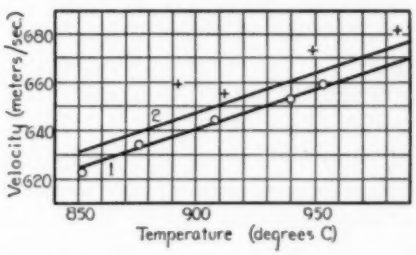

Fig. 2. Velocity of sound in air, Steven's measurements. Curve 1, (circles) measured, 2 cm tube. Curve 2, calculated, 4 cm tube. Crosses are measured values for 4 cm tube.

Review of the evidence adduced in the preceding shows that in the measurements of greatest accuracy, the Helmholtz-Kirchhoff equation is very closely substantiated; certainly within the limit of error. These measurements involved moderately high frequencies and large tubes. If the experiments at low frequencies and with very small tubes (excluding, of course, those by the dust-figure method) are given much weight, it is possible to claim that the theory is not exactly correct and fails under conditions that exaggerate its imperfections. Even in these cases, indications were found that errors of method, rather than of the theory, are responsible for the apparent discrepancies. It is believed that more accurate and complete measurements, which will be required before the question is finally settled, will show close correspondence with the theory. Any future measurements should include the field of high temperatures where the present evidence is indecisive.

Of the several methods which have been employed for making the tube-correction, that depending upon graphical or algebraic application of the inverse diameter law is to be preferred, provided the measurements are of enough precision to give the required accuracy of extrapolation. The reason for this preference lies not only in the fact that it is independent of any detailed theory, but also in that it corrects partially for any errors of method that vary with the diameter of the tube. This method assumes, of course, that measurements with two or more tubes are available. When this is not the case, or if enough precision is not attainable for accurate extrapo-

lation, the Helmholtz-Kirchhoff equation should be applied. The question of precision of measurements is important because the error in the calculated result by the two-tube method is necessarily greater than the experimental uncertainty of measurement in either of the tubes alone. While it would appear to be always possible to reduce this error to any desired limit by a sufficient number of measurements, a practical consideration arises that makes this difficult, at least with some methods. Thus it was found in the measurements already cited[8] that the results in the smaller tubes were less reproducible than in the larger. It seemed in this case that more reliable values could be obtained by applying the Helmholtz-Kirchhoff equation directly to the measurements of greatest accuracy (those in the large tubes). The same appeared also to be true (cf Ref. 8, p. 648) of the work of Grüneisen and Merkel.[7]

The method of correction adopted by Dixon, Campbell and Parker[5] and by Shilling,[13] consisting in the "calibration" of a tube by comparison of the velocity measured in it with a standard accepted value for the free gas, employing their theoretical constant C of Eq. (2) to determine a "tube constant," is open to rather serious objection. In the first place, it requires that both the standard of comparison and the calibrating measurements be of an accuracy and reliability not attained in many existing measurements. All of the error in the large velocities, which, in view of the difference commonly found in results of different observers of the same quantity is not to be estimated from the apparent precision of any one set of measurements, is thrown into the small correction term, making possible very large percentage errors in it. As these errors are again magnified in calculation of specific heats, the question of the attainable accuracy is extremely serious. Secondly, if the Helmholtz-Kirchhoff equation is not correct and the properties of the tube have to be considered, which is urged by Partington and Shilling as one of the reasons for its use, this method becomes theoretically unjustified. It is obvious, for example, that if the thermal conductivity and specific heat of the tube walls cannot be considered infinite as compared with the gas, that the Helmholtz-Kirchhoff expression involving the conductivity in the gas will no longer hold. The calibration made with one gas could, therefore, not be used with another. Moreover, the properties of the tube change with temperature, and this, together with the variation of the function covering the properties of the gas, prevents the use of a calibration made at one temperature at any other. The method of correction employed, therefore, by these authors in their high temperature specific heat work tacitly presupposes the validity of the Helmholtz-Kirchhoff assumptions.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
BERKELEY, CALIFORNIA,
October 11, 1928.

AN OPTICAL STUDY OF ADSORBED FILMS

By J. H. Frazer

Abstract

The optical method of Rayleigh and Drude for the study of surface "transition layers" (Uebergangsschichten) has been experimentally modified so as to give greater accuracy, and has been applied to the study of adsorption on glass. Various substances were investigated, and of these only two, water and methyl alcohol, showed definite adsorption. Curves for these, plotting thickness of adsorbed layer against partial pressure, are given. Up to 5 or 6 mm pressure there is no detectable adsorption of water vapor (apart from the probable presence of the first mono-molecular layer). From then on there is a cluster formation which results in a gradual covering of the surface until at 12.5 mm pressure there is another mono-molecular layer present. Above 13 mm there is strong condensation. The results for methyl alcohol were similar. Adsorption began at 30 percent saturation and continued linearly up to 90 percent saturation pressure, when strong condensation set in. It is pointed out that the method is applicable to the study of surface conditions at the interface between any two phases.

A METHOD for detecting adsorbed films was sought which should be free from the objections which obtain in the case of the previously used methods. These methods are:

(a) *Langmuir's method.* In this method a known quantity of the gas to be adsorbed is contained in a bulb of known volume, this bulb being connected by an initially closed stop-cock with a second bulb, also of known volume in which there is contained a large bundle of the surfaces on which the adsorption is to take place. When the stop-cock connecting the two bulbs is opened, the gas expands, filling both bulbs, and from a knowledge of the original pressure and the volume of each bulb, the pressure which should be finally established can be calculated by Boyle's Law. Any decrease in the observed pressure below the theoretical will then be accounted for by adsorption on the adsorbing surfaces and walls of the second bulb. To eliminate this second factor, an exactly similar run is made, but without the adsorbing surfaces. The difference between the adsorption observed in two cases is, then, that due to the adsorbing surfaces. This method can only be used at pressures far below saturation, since at the higher pressures the pressure change is so small, compared with the total pressure, as to be completely masked.

This constituted one objection for our purposes; a second being that we wished later to study adsorption on surfaces available only in rather restricted areas.

(b) The method of Frazer and Patrick, which takes the pressure-temperature curve of the adsorbed gas in a bulb of the adsorbing material around saturation pressures, the degree of rounding off of this curve on

passing from the Charles Law curve to the vapor pressure curve determining the amount of adsorption. This method is limited in that it is restricted to a region close to saturation (it could not detect adsorption below one molecular layer) and as in Langmuir's method, by the large surface required and by the long time necessitated to make measurements.

Since it was desirable to make measurements right up to saturation pressures, and since sometimes only small areas of adsorbing material were available, a method was sought which should fulfill the following requirements: (a) It must be applicable at all pressures; (b) It would be highly desirable to have it applicable to small surfaces of adsorbing material; (c) It should be accurate to at least 1 A.U.; (d) It must be workable in a reasonably short time.

A method fulfilling these requirements was found in an optical method, the theoretical foundations of which were laid by Drude,[1] and which was first applied by Lord Rayleigh.[2] It has since been used by Raman and Ramdas,[3] recently by Ives and Johnsrud,[4] and very recently by Ellerbrock.[5]

The theory of the method is as follows: When light, polarized at 45° to the plane of incidence, falls on a perfectly abrupt boundary between two media at the polarizing angle, the reflected beam should be completely plane-polarized at right angles to the plane of incidence. Experimentally, when light, under these conditions, is reflected at the polarizing angle from any surface whatsoever, it is observed that these conditions are not quite strictly fulfilled. There is always a slight ellipticity to the reflected beam, the major axis of the ellipse lying perpendicular to the plane of incidence. Drude explained this theoretically by assuming that the transition from the refractive index n_1 of the first medium to the refractive index n_2 of the second medium is not abrupt as required by this elementary theory, but is gradual, passing over continuously from one medium to the other. This region in which the refractive index is gradually changing is called "a transition layer." The formula that he gives is as follows:

$$\rho = \frac{\pi}{\lambda}\left(\frac{\epsilon_1 + \epsilon_2^{1/2}}{\epsilon_1 - \epsilon_2}\right)\int \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon} dz$$

where ρ is the observed ellipticity, ϵ_1 and ϵ_2 the refractive index of the 1st and 2nd medium, ϵ that of the transition layer, λ is the wave-length of the light used, and Z the position in the transition layer, measured from the junction of the transition layer with medium number two. Experimentally, the effect is detected as follows:

The incident light, plane polarized at 45° to the plane of incidence, is reflected at the polarizing angle, and the analysing nicol set to the minimum, which is different from zero because of the ellipticity. A Babinet compensator

[1] Drude, Lehrbuch der Optik.
[2] Rayleigh, Phil. Mag. [6] **23**, 431 (1903); [5] **33**, 1 (1800); [6] **16**, 444 (1896).
[3] Raman and Ramdas, Proc. Royal Soc. **A108**, 561 (1925).
[4] Ives and Johnsrud, Journal of the Optical Soc. **15**, 374 (1927).
[5] Ellerbroek, Arch. Neerland, Sci. III **A10**, 42–90 (1927).

is introduced, the ellipticity of the reflected light compensated, and the ratio of the maximum to the minimum, the ρ of Drude's formula determined. Ellerbroek could determine an adsorbed layer of about 1 A.U., corresponding to a displacement of his compensator of about 0.001 mm, but he trusts his readings only to 0.01 mm displacement of the compensator.

In the present work, the following changes were introduced: (1) A Point-o-lite lamp was used, which was steadier and more convenient than the sunlight used by most previous investigators. (2) Instead of compensating the ellipticity of the reflected light, as has been done previously, we find the ellipticity by measuring the ratio of the two axes of the ellipse photometrically. This is done by using unpolarized incident light and analyzing the reflected light with a nicol prism which was set first in, and then perpendicular to, the plane of incidence (maximum and minimum of light intensity). The maxima and minima so transmitted by the nicol were measured photometrically, and their ratios were the ellipticity.

The advantages of our method were: (a) Greater sensitivity. Whereas Ellerbroek claims only 10 A.U., our probable error was less than 3 A.U. (b) Greater simplicity. By measuring the ellipticity photometrically, we have dispensed with the Babinet compensator and with the polarizing nicol. This simplifies the operation very much, since photometric readings are much easier to make than adjustments of a Babinet compensator. (c) Our set-up is considerably less expensive. The Babinet compensator is a highly specialized and very expensive piece of apparatus, whereas a very good photometer can be made easily.

An optical bench holding the Point-o-lite optical set-up, condensing lenses, and collimating lens was mounted on a divided circle over the axis of which the reflecting specimen was placed. The analyzing nicol and photometer were mounted on another table, far enough away from the rest of the apparatus to eliminate stray light. In operation, the procedure was to find the polarizing angle, set the analyzing nicol to the minimum, read the photometer, set to the maximum, read again, and the square root of the ratio of intensities so found was the ρ of Drude's formula.

The photometer deserves special mention. It was of the type in which the field is split by a 45° mirror, the mirror reflecting the light from a ground glass illuminated by the photometer light, the light to be measured passing by the edge of the mirror. The comparison was obtained by adjusting the distance of the photometer light from the ground glass. The photometer lamp itself was a small flashlight bulb, run at a constant current somewhat below its rated capacity to reduce the danger of burning it out. In some cases screens, transmitting a known percentage, had to be introduced in order sufficiently to reduce the intensity. These screens were calibrated on the instrument itself. The readings taken were the simple inverse of the photometer lamp distances, since it was the amplitudes which were desired. The absolute value of the readings were of no importance, since the ellipticity appears as the ratio of two readings. The following presented itself as a very serious experimental difficulty. Since the reflecting surface was

rarely optically flat, the half of the field illuminated by the light to be measured differed so in texture from the comparison field, that no match was possible. A timely suggestion of Professor Pfund's eliminated this entirely. The light beam, after reflection and passage through the nicol, was brought to a focus on a piece of lightly ground glass by a good achromatic lens. A similar lens was placed at its principal focal distance from the illuminated spot, and the parallel beam of light so formed was extremely uniform and could be matched with ease.

The sources of experimental error in this method are as follows: (a) A possible error in the determination of the polarizing angle; (b) A possible error in the setting of the analyzing nicol prism; (c) Possible double refraction of the glass window through which the light had to pass after reflection in the case of the vacuum work; (d) The error in the photometric measurements.

If we take Drude's equations

$$\frac{R_p}{E_p} = \frac{\cos\phi(\epsilon_2) - \cos\chi(\epsilon_1)^{1/2} + i(2\pi/\lambda)\left[p\cos\phi\cos\chi - (l - q\epsilon_2\sin^2\chi)(\epsilon_1\epsilon_2)^{1/2}\right]}{\cos\phi(\epsilon_2)^{1/2} + \cos\chi(\epsilon_1)^{1/2} + i(2\pi/\lambda)\left[p\cos\phi\cos\chi + (l - q\epsilon_2\sin^2\chi)(\epsilon_1\epsilon_2)^{1/2}\right]}$$

$$\frac{R_s}{E_s} = \frac{\cos\phi(\epsilon_1)^{1/2} - \cos\chi(\epsilon_2)^{1/2} + i(2\pi/\lambda)\left[l\cos\phi\cos\chi(\epsilon_1\epsilon_2)^{1/2} - p + l\epsilon_2\sin^2\chi\right]}{\cos\phi(\epsilon_2)^{1/2} - \cos\chi(\epsilon_1)^{1/2} + i(2\pi/\lambda)\left[l\cos\phi\cos\chi(\epsilon_1\epsilon_2)^{1/2} + p - l\epsilon_2\sin^2\chi\right]}$$

and introduce a variation, α, in the setting of the nicol prism, and a variation, β, in the setting of the polarizing angle, we obtain the following formula expressing the dependence of the observed value of the ratio $(R_s/R_p)_{obs}$ on these two quantities

$$(R_s/R_p)_{obs.} = (R_s/R_p)(1+\beta+\alpha)$$

This formula is correct except for a function of the refractive index which would not change the expression markedly, and for higher powers of α and β. From this we see that an error of 0.01 percent, which means a variation in either of these two quantities of 0.3° means an error in R_s, and consequently in ρ, since the maximum is not appreciably affected, of about 10^{-4}, and this is about the limit of the accuracy with which the photometric measurements can be made.

Now a change of 10^{-4} in ρ means, in dealing with water layers on glass, a change in the adsorbed layer of 0.3 A.U. Accordingly this is the limit of accuracy obtainable in this case. It is interesting to note that in the case of the setting of the polarizing angle, and also in the setting of the nicol prism, it was observed experimentally that the calculated allowable deviations experimentally produced no change in the reflected intensity.

The lowest mean deviation in the photometer settings which could be obtained at these low intensities was from 1 to 2 percent. Accordingly groups of 6 to 12 settings were averaged together. These groups showed mean deviations less than 1 percent, and it is believed that they are accurate to 1 percent. It is the group of 6 to 12 settings which will hereafter be referred to as a reading.

In order to test for the possible double refraction of the glass window, a specimen was taken which showed a very good minimum, and its ellipticity was determined in the apparatus and in air. This was repeated several times and, in all cases, the results were smaller than the experimental error.

Preparation of Adsorbing Surfaces

Various methods of obtaining good glass surfaces were tried. Polishing seemed too tedious a process, and the contact with the abrasive would have left the glass in a doubtful condition. Thin blown pieces of glass showed a fair surface condition, but difficulty was experienced in eliminating the reflection from the back surfaces. Glass exposed to a flame showed a very bad surface condition. Finally, on a suggestion of Professor Pfund's,the glass was cracked in the following way. A piece of plate glass was scratched at its edge for about an inch, and a crack started. Then a steady pull at the cracked edge would produce a break which would be sometimes, over areas as great as 1/2 cm^2, almost as good as plate glass. Numerous pieces of glass cracked in this way showed consistent small ellipticities of about 0.01. Expressed as a transition layer, this would mean a layer about 30 A.U. thick. To calculate this value, we considered the region or layer occupied by the hills and depressions of the glass surface as a region with a statistical refractive index approximately the average of the refractive index of the glass and air. This is legitimate since the irregularities here considered are small in comparison with the wave-length of light. The ellipticity of the light reflected from a piece of glass broken in air in this way showed no change with time, and also showed no change on being placed in a fairly good vacuum (10^{-6} mm) on a McLeod gauge. A piece of glass could be allowed to stand exposed to the atmosphere for as much as two days without showing appreciable change, and could probably have remained longer, although this was not tried. One experiment was tried in which it was attempted to crack the glass in a vacuum, and the value of the ellipticity so obtained was not changed on admitting air to within the experimental error, which in this case, however, was rather large, due to the bad surface produced because of a lack of technique for cracking the glass in vacuum. In any case, the hot wire used to crack the glass probably evolved enough gases to vitiate the experiment. The reason for mentioning this is that Dr. Langmuir, with whom we had the opportunity of discussing the subject, believes that in all the following work there is already present a mono-molecular layer of water held very tightly by the secondary valence bonds of the various constituents of the glass, and that whatever adsorption we observe would be a second or subsequent layers.

Adsorption

Previous theories. Langmuir had suggested in contradiction to previous theories, especially of Polanyi, that only mono-molecular layers of gases were adsorbed below the saturation point. His experiments on the adsorption

of nitrogen, oxygen, methane and carbon monoxide on glass and mica confirmed this view.

The same result follows from the experiment of Frazer and Patrick, who took the pressure-temperature curve of a volume of water vapor enclosed in a freshly blown glass bulb.

They showed that there was no rounding off of the curve such as would have been caused by adsorption of considerable amounts of water, but, that in passing from the Charles law to the vapor pressure curve, they pass not to the vapor pressure curve of pure water, but to a somewhat lower vapor pressure. They attributed this to a solution in the water of the alkali from the glass, and actually succeeded in titrating the amount of this alkali present, and determining the concentration of alkali necessary to produce the vapor pressure lowering below that of pure water which they observed. This work was all done with freshly blown glass surfaces, always protected from exposure to water vapor. However, the situation was quite different when these surfaces were allowed to stand in contact with water vapor for any length of time. Under these circumstances, the curve showed considerable rounding off on passage from the Charles Law to the vapor pressure curve, and consequently considerable adsorption. But correlative with this activation of the glass, it was shown that sufficient alkali had been dissolved from the glass to turn phenolpthalein pink, and these results seemed to indicate that the activation consisted in dissolving the alkali from the complex silicate of the glass, leaving there something analogous to silica gel, which readily adsorbs great quantities on account of its large surface.

Investigations with the new method. The first results obtained were those on water vapor. If water vapor be admitted to a specimen of glass standing in vacuum, there is no observable change in the ellipticity until pressures of around 6 mm are reached. From then on the ellipticity increases almost linearly with the pressure, until at about 12.5 mm pressure there is a sharp discontinuity, the curve from then on again increasing almost linearly with the pressure, but much more sharply than before. The calculated film-thickness at which this break occurs is about 3.0 A.U. At any stage in this process, the system can be re-evacuated, and the adsorbed film, as measured by the ellipticity of the reflected light, can be completely removed; the ellipticity can be returned to its original value. More than this, the thickness of film is a function only of the pressure, and not of the past history of the specimen. The time taken to establish equilibrium at any value of the pressure, either ascending or descending, is certainly less than the time required to read the instrument, and this was, on an average, about 3 min.

It follows, therefore, that up to 5 or 6 mm there is no detectable adsorption (apart from the probable presence of the first mono-molecular layer). From then on there is a cluster formation which results in a gradual covering of the surface until at 12.5 mm pressure there is another mono-molecular layer present. Above 13 mm there is strong condensation. That this occurs below saturation pressure of 18 mm is accounted for on the basis of Frazer and Patrick's work as a hydration of the glass by the first layer of water,

and a consequent lowering of the vapor pressure of the water by the dissolved alkali. However, one objection at once comes to mind in that, if the system is again exhausted, the water can be removed from the glass completely, restoring the ellipticity to its original value. This would indicate that the alkali recombined with the glass. An attempt to test the existence of a possible decomposition of the glass was made in the following way:

Water vapor was admitted which contained a small percentage (about 1 percent) of hydrochloric acid gas. When it was attempted to pump off this layer, it was found that there remained a residual ellipticity, indicating about 9 A.U., which could not be removed by any amount of pumping. It is thought that the hydrochloric acid combined with the alkali of the glass leaving a film even when all the water was pumped off. It is realized quite well that this is open to the objection that possibly the hydrochloric acid produced the decomposition instead of rendering permanent an already produced decomposition. However, it is an indication.

The second substance tried was methyl-alcohol, which showed in general the same type of curve showed by water, namely a linear increase in ellip-

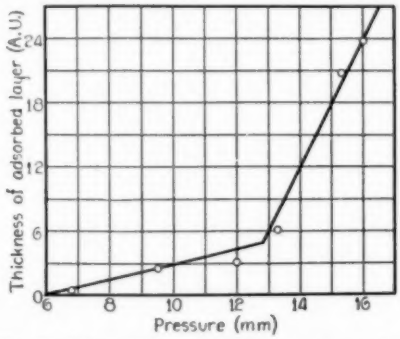

Fig. 1. Adsorption of water vapor on glass.

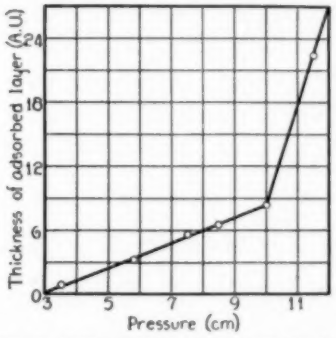

Fig. 2. Adsorption of methyl alcohol vapor on glass.

ticity starting in roughly at about 30 pecent saturation pressure, and continuing up to within about 90 percent of saturation. Then there was an abrupt break in the curve, the ellipticity from this point on increasing very rapidly. It is not quite understood what the significance of these results is. The break occurred at about 9 A.U., a value considerably larger than the normally accepted value for the size of a methyl-alcohol molecule. However, it must be remembered that if there is any asymmetry of the molecules they will, under these conditions of adsorption, orient themselves with a long axis perpendicular to the glass surface. A second fact which is hard to understand is the presence of the steep part of the curve indicating either a large amount of adsorption, very near saturation, or a double decomposition of the glass of the same type as that occurring with water and glass. Subsequently, this will have to be tested for. The curves and data for these two substances are presented in Figs. 1 and 2.

Other things were tried, and in all cases except one they were selected because of a high value of their dielectric constants, but in all cases the results

were negative. In fact, it was even impossible to force these substances to condense on the glass at saturation pressures. The substances falling in this class were nitromethane, acetone, toluene, and formaldehyde.

This method enjoys a distinct advantage over other methods in that it is possible to detect, by its use, adsorption at the boundary of any two phases, and is not necessarily restricted to the solid-gas interface. One experiment was tried to detect adsorption at a solid-liquid interface. The light was reflected from a piece of heavy lead glass immersed in a light gasoline previously purified by the department of organic chemistry. The ellipticity was measured and then a small quantity (about 2 percent) of oleic acid was added. The polarizing angle was then redetermined, since the oleic acid added changed the refractive index of the gasoline. The observed change in ellipticity was about 0.0005, which means a layer of about 4.5 A.U.

The author wishes gratefully to acknowledge the timely assistance of Professor A. H. Pfund in the optical set-up; and wishes also to express his indebtedness to Professor K. F. Herzfeld, who suggested the problem, and supervised its growth and completion.

THE JOHNS HOPKINS UNIVERSITY,
June, 1928.

BOOK REVIEWS

Colloid Chemistry. THE SVEDBERG. (Professor of Physical Chemistry, University of Upsala) Second Edition. Pp. 302, 167 figs. American Chemical Society Monograph Series. Chemical Catalog, New York, 1928. Price $5.50.

The first edition of this book appeared in 1924 and was based upon a series of lectures given at the University of Wisconsin during the spring and summer of 1923. The rapid advance of colloid chemistry especially along the lines of quantitative measurements, has necessitated the present revision.

Probably no living worker is more qualified to speak with authority in regard to certain of the physical phases of colloid chemistry than is Professor Svedberg, for it is in his laboratory and under his direction that many of the more exact studies have been carried out and intricate apparatus especially adapted to colloid studies has been designed.

As the author notes in the preface, a very considerable part of the book is devoted to those special fields which have been intensively studied in his own laboratory. While this causes the book to be somewhat unbalanced, it at the same time makes it more valuable in that the fields which are covered are covered in an authoritative manner.

The formation of colloidal sols is considered at length. Much of the special apparatus designed by the author is figured, and detailed accounts of precautions which must be taken are given.

A discussion of "The colloid micelle as a molecular kinetic unit" occupies nearly half of the volume. In addition to bringing up to date the observations of Brownian movement and ultra-microscopic studies we have here for the first time an adequate discussion of the exceedingly important studies which Svedberg has carried out with his ultra-centrifuge, the latest model of which is of the oil turbine type capable of developing a centrifugal force 94000 times gravity and running without appreciable vibration. By the use of this instrument he has determined with a high degree of accuracy the particle weight of the colloid micelles in various systems.

While the discussion of the lyophobic sols is excellent, the reviewer feels that the space and discussion devoted to lyophilic gels (16 pages) is altogether inadequate so that the book will have a limited appeal to those who are primarily interested in the biological application of colloid chemistry. For example, the Donnan equilibrium is dismissed with little more than casual mention.

The physicist and the physical chemist will, however, find in this volume much which will assist them in further evaluating in quantitative terms the energy relationships and energy exchanges characteristic of colloid systems.

The day for empirical observations in colloid studies has passed. The studies of the future must yield quantitative data and the theory as presented in this volume will assist to that end.

ROSS AIKEN GORTNER

Lehrbuch der Physik. ARNOLD BERLINER. Fourth edition. Pp. 658, 802 figs. Julius Springer, Berlin, 1928. Price 19.80 RM.

This well-known elementary treatise on Physics is characterized by a clear and accurate presentation of the fundamentals with a minimum of mathematical analyses. It is surprisingly complete in scope for though his treatment is elementary the author does not hesitate to discuss subjects which are usually omitted from an elementary text such as the general theory of relativity and the quantum theory of the structure of the atom.

A particularly valuable feature of the book is the attention which has been paid to the applications of Physics to the problems of engineering, chemistry and physiology. In this, the fourth edition, the number of these applications has been increased and new sections have been added dealing with Corioli's motion, motion of the top, crystal structure, astrophysics and

geophysics. Unfortunately, there are almost no references to the literature. The paper, printing and binding, measure up to the high standard of the publishers.

JOHN T. TATE

Annual Tables of Constants and Numerical Data. Chemical, Physical, Biological and Technological. Volume VI (1923–1924), two parts, quarto, containing XXXIV pp. of general information and 1674 pp. of numerical tables and curves. Gauthier-Villars et Cie, Paris; McGraw-Hill Book Co., New York, 1927–1928. Price, unbound 530 fr., bound 610 fr., ($25.00).

This volume is the first of the second series of the Annual Tables. It contains all the numerical data that has appeared in scientific publications throughout the world during the year 1923–1924. As compared with previous volumes, Volume VI offers a number of improvements and, in particular, the addition of detailed indexes to some of the more complex chapters and of lists of the substances or systems studied in many of the chapters. In the final chapters of the Volume on Engineering and Metallurgy the text is given in English as well as in French. The publishers state that this improvement will be made throughout the whole of Volume VII which is to appear in 1929.

JOHN T. TATE

A First Course in Physics for Colleges. R. A. MILLIKAN, H. G. GALE, and C. W. EDWARDS. Pp. 676+xlii, 583 figs. Ginn and Company, Boston, 1928. Price $3.72.

This college text is an outgrowth of the "First Course," by Millikan and Gale, which has been so extensively used for many years, and contains much additional material, some slight rearrangements, and considerable rewriting. It is written in a clear and simple style, and dogmatic statements are avoided as much as can be without emasculating the whole structure, the result being to stimulate an understanding rather than a memorizing of the subject. As textbooks go, it may be classed as a conservative. The fundamental definitions and concepts are given in the traditional form, there are no radical rearrangements of the accustomed sequence of material, no radical omissions of familiar terms or topics, nor any extensive consideration of the newest speculations and points of view. For example, while considerable space is given to the discussion of very recent developments of applied physics, the word "quantum" receives only the briefest mention on the very last page. Of course, any considerable introduction of current speculations into an elementary text is fraught with danger—it tends toward vagueness and uncertainity and stimulates a certain type of pupil to indulge in useless imaginings rather than to master what has been accomplished. Also, a book which does much of this is certain to be relatively difficult to use. Teachers of physics have on the whole, to judge by most textbooks, been slow to introduce new material. One hears of elementary classes in psychology warmly debating the pros and cons of behaviorism, but one never hears of elementary students of physics taking sides for or against the quantum theory. Not that I believe that physics teachers should or could develop a corresponding animation, which must at best be extremely superficial, in the discussion of physical questions, but the judicious introduction of the new and unsettled does create an atmosphere of growth and development. In the text under discussion, this atmosphere is fostered rather by the description of new applications than by consideration of new theories. The illustrations, which are profuse, are not only of the usual diagrammatic kind, but include a number of half tones of instruments and machines and portraits of physicists. The latter are accompanied by brief biographical sketches and serve excellently to give a touch of human reality to names otherwise associated only with abstract laws of notable advances. The "teachableness" of a book can really be determined only by trial. Lacking such a test one can only judge from general impressions, which in this respect are altogether favorable, and from this and the confidence inspired by the experience of the authors, predict that the book will be found very usable, and a valuable addition to the list of first year college texts.

C. E. MENDENHALL

Handbuch der Experimentalphysik. Wien-Harms, Band VII. Teil.: 1 **Krystallographische und strukturtheoretische Grundbegriffe.** P. NIGGLI. Pp. 317, 131 figs. Akademische Verlagsgesellschaft m. b. H., Leipzig. 1928. Price, bound 32.50 RM.

The inclusion of this monograph in a series on experimental physics is somewhat misleading since it contains no description whatever of experimental methods or results. What it does contain is the mathematical basis on which the complete analysis of any particular crystal structure must rest. This is, of course, wholly independent of the special methods by which the structure in hand may be differentiated from others. Among these methods the study of x-ray diffraction is powerful but not, as the author properly emphasizes, especially in the last chapter, sufficient in itself to discriminate all the possibilities.

The first five chapters comprising over two-thirds of the text contain but few novelties for the student of mathematical crystallography. The treatment of rotations as compound reflections is perhaps the most striking of these. The reciprocal lattices also receive an unusual amount of attention at a very early stage in the argument. By focusing attention upon the quadratic form which characterises a lattice, and by deferring the classification of lattices on the basis of symmetry, the difficulties due to pseudo-symmetry are clearly and forcibly presented. This part of the book amplifies and extends the author's earlier presentation (Geometrische Kristallographie des Diskontinuums, Borntraeger, Leipzig, 1919) but does not replace it, the detailed description of the 230 space-groups not being reprinted here.

Two of the remaining three chapters are devoted to subjects that have developed very recently and are still far from completed. These concern the analysis of a crystal structure into subordinate structures. In one kind of analysis the elements consist of structurally equivalent points, each element therefore being associated with a lattice coextensive with the crystal. This sort of element has particularly simple properties in x-ray diffraction, a single vector replacing it in the calculation of intensities. The shortest methods for the specification of this vector are fully explained. In the other kind of analysis the elements are selected on the basis of propinquity, so that each element is a coherent (but not necessarily finite) group, the members of which have peculiarly close physical relationship sometimes explicable on chemical grounds. In connection with the latter type of analysis the topological problems involved in the packing of hard spheres—in the first instance of equal radii—are introduced. The author points out in these most interestingly written parts of the book that a great deal of time may eventually be saved by the tabulation, at present only begun, of all the possibilities. His previous record as a systematizer promises well for the completion of this ambitious program.

The book contains an imposing array of tables and formulas for the convenience of the computer from crystallographic data and full definitions of all technical terms. The index is so good that this information is really accessible and the frequent emphasizing of important words or phrases makes it relatively easy to pick out the desired part of a page. This last-mentioned feature is important because the style in the first part of the book is so repellantly monotonous that reading much of it at a time is fatiguing.

The paper and type are good, the binding is rather flimsy for a work of reference. No typographical or other errors of any importance have been noted by the reviewer.

L. W. McKeehan

Probability and its engineering uses. Thornton C. Fry. Pp. 476, 48 figs. D. Van Nostrand, New York, 1928. Price $6.00.

The reviewer is not an authority on the theory of probability; rather these remarks are written from the standpoint of one whose knowledge of the subject is largely derived from the study of the book under consideration. It is an excellent book and provides just the sort of introduction to the subject that one wishes for. There is a certain haughtiness among "pure" physicists which often leads them to avoid books with any suggestion of engineering about them. He who yields to such an impulse in this case certainly does himself and the author an injustice.

The book was originally prepared in connection with the "Out-of-Hours Courses" which are given by staff members to the younger research workers at Bell Telephone Laboratories. Later a course based on it was given by the author at the Massachusetts Institute of Technology.

The first seven chapters are occupied with a clear and interesting presentation of the principles of the subject. The exposition is characterized by its not assuming more mathematical knowledge than upper classmen in good engineering schools are apt to have. For example, where distribution functions in several variables are under discussion there is ample treatment of the Jacobian of a transformation insofar as it is needed. There is an emphasis on physical applications throughout; in the chapter on distribution functions Maxwell's original derivation of the law of distribution of velocities in a gas is given.

Chapter VIII, "The distribution functions most frequently used in engineering," contains an excellent account of the inexactness of the Gauss error curve as a represenation of the binomial probabilities. The limiting form of the binomial law which gives rise to Poisson's law is fully treated and an ample account of its many and varied applications is given. Chapter IX, "Curve fitting," has a valuable account of the Pearson test for "goodness-of-fit" and the principles underlying inference from statistical data. Chapter X, "The theory of probability as applied to problems of congestion," introduces the reader to one of the chief concerns of the telephone industry with probability theory, and a field of application which should be of importance in other industries.

Chapter XI, "Fluctuation phenomena in physics," gives the Boltzmann collision method of deriving the law of velocity distribution of gas molecules and deals with the important questions of density fluctuation and the Schottky effect. The tables are a noteworthy feature. They include factorials of 1 to 200, log factorials of 1 to 1200, binomial coefficients C_n^m up to $m=100$, the error integral and its derivatives to the sixth, the Poisson law and Pearson's goodness-of-fit criterion.

The wide-spread use of the notions of probability in all natural science as the basis of inference from observations and the important role they play in some of the most fundamental thought in physics makes it highly desirable that there be more formal study and teaching of probability theory among physicists. This appears to be the first book on probability theory to be written with the needs of physicists always in the foreground and is so well done that it deserves extensive use by us.

E. U. CONDON

Introduction a la théorie des quanta. M. BOLL and C. SALOMON. Pp. 457, 46 figs. Gaston Doin et Cie. Paris, 1928. Price 85 fr.

One has to understand the words "Introduction to" in the title as referring to a presentation of the *classical* theoretical physics which is most directly connected with quantum theory. So understood the book is quite useful. The quantum theory is confined to the "Avant-propos" of fifteen pages in which the problems which concern quantum physics are outlined. The new mechanics which has given the subject a whole new complexion since 1925 is dismissed in three pages.

The first two parts (254 pages) contain en excellent treatment of the principles of classical dynamics after the methods of Hamilton and Jacobi. Contact transformations, Stäckel's theorem, Hamilton's principle, multiple periodic systems, integral invariants and adiabatic invariance are treated clearly.

The third part (203 pages) similarly gives an account of classical electron theory emphasizing the parts of most use in quantum theory but consistently refraining from any further discussion of quantum physics and the difficulties of classical theory than is given in the introduction.

E. U. CONDON

Vorlesungen über Vektor-Rechnung. MAX LAGALLY, Professor of Mathematics at the Technischen Hochschule, Dresden. Pp. 358. Akademische Verlagsgesellschaft, Leipzig, 1928.

This is the best text on vector analysis which has come to the reviewer's attention in a number of years. The author uses Gibbs' notation employing dots and crosses in place of the awkward parentheses and brackets so generally adhered to by continental writers, although later on he introduces *grad*, *div*, *rot* as alternatives to Gibbs' more significant *del* notation.

The first chapter takes up the elementary algebra of vectors and dyadics. The next chapter treats the differentiation of vectors with respect to a scalar parameter, and contains

numerous applications to the geometry of surfaces and to mechanics. Chapter 3 deals with the theory of fields. The gradient, divergence and rotation are defined, Gauss' and Stokes' integral theorems deduced, and applications made to hydrodynamics and potential theory. Next comes a chapter on the further development of the theory of dyadics, taking the reader as far as the Cayley-Hamilton equation. This is followed by a chapter illustrating the use of dyadics in mechanics—particularly in connection with rotation and elasticity. The last three chapters are on transformation theory, vectors in a Riemann space, and complex numbers, including a brief account of quaternions.

LEIGH PAGE

Struktur der Materie, Band VII, Graphische Darstellung der Spektren von Atomen und Ionen mit Ein, Zwei und Drei Valenzelektronen. W. GROTRIAN. Part I Pp. 245, 45 figs.; Part II Pp. 168, 163 figs. Julius Springer, Berlin, 1928.

As the title implies, the main feature of this volume is a collection of graphical representations of the spectra of one, two and three-valence-electron atoms and ions. These diagrams, 163 in number, constitute the whole of part II. Atomic structure diagrams, of the type introduced by the author, are given for all one, two and three electron systems whose spectra have been analysed. In addition there are included a complete set of Moseley diagrams as well as graphs illustrating the irregular and regular doublet laws and other features of these spectra.

Part I contains descriptive material written around the diagrams of the second section. Since previous volumes of the series of which this is the seventh volume have treated the theoretical problems of spectra, the author omits as far as possible all mathematical and theoretical discussions and confines himself to the detailed description of the individual spectra for which diagrams are given. This leads to a slight lack of unity which in some cases seems unnecessary. Thus it is difficult to understand why the PP^1 groups of the three electron systems should be placed in separate diagrams rather than in the general diagrams of these systems along with the ^1D and ^1S terms which arise from identically the same electron configuration as the P^1 terms.

Another serious defect, from the standpoint of the reader who is not thoroughly familiar with the older notations, is the use of the original Paschen notation throughout the first part rather than the generally accepted Russell-Saunders notation. The diagrams of the second part are labeled with both notations.

The diagrams of part II, in particular, should prove very valuable to anyone wishing to locate rapidly the position of any line in the term system of these atoms or ions.

I. S. BOWEN

An Outline of Physics. ALBERT EDWARD CASWELL. Pp. xiv+773, 441 figs. Macmillan Company, New York, 1928. Price $4.25.

We suspect that when the three authors of a certain much-discussed "general physics for colleges" published their first edition in 1923, they unconsciously played the part of a Cadmus, in sowing the dragon's teeth. Be that as it may, the harvest of rival textbooks, bearing banners emblazoned with "modern physics," emancipated from the traditional manual of arms of their forbears with respect to order of topics, and characterized by an informal conversational style, is most impressive. It is a manifestation of the response of the physicist to the universal dissatisfaction with educational methods of the past. The physicist's restlessness is of course aggravated by the growing pains with which his science is at present beset.

The book before us affords a good example of present-day tendencies. Such terms as "electron," "orbit," "quantum" are of frequent occurrence throughout the volume, and the manner of introducing them and other modern concepts is in the main natural and logical. Less fortunate, to the reviewer's mind, is the literary style, which savors frequently of the colloquialisms and off-hand analogies of the "quiz section." Electrons are "pumped," they "hurl themselves" against targets, nay they "bounce up and down" like tennis balls! The too frequent avoidance of the accepted vernacular of physics in favor of that of the newspaper headline tends to defeat one of the objects commonly sought in teaching natural science.

Perhaps the outstanding characteristic of Professor Caswell's book is the quite unconventional order of presentation. To quote from the preface: "In the earlier chapters he has brought together essential facts from the whole field of physics. In the central portion of the book these facts are coordinated by well-established theories, and new facts suggested by the theories are brought to light. Some of the more recent developments which may still be regarded as matters of conjecture or interpretation are considered toward the end of the book." Most of the elementary college texts of the past have attempted to serve as systematized reference-books on the fundamentals of physics, while at the same time meeting certain—or uncertain—pedagogical requirements. Professor Caswell evidently considers it impossible for one and the same book to play both of these rôles. He has therefore undertaken a radical rearrangement of material, designed "to make the subject matter of physics more vital and more interesting." The result is, in effect, a sequence consisting of a short summary of the principal laws of physics, followed by a brief course in the subject, adhering in a general way to established custom and occupying over half of the book; and finally a treatment of the more advanced topics in the various branches. This method offers obvious advantages; only time and experience can tell whether it will supplant the older "watertight compartment" method. The fact that information on so many topics is scattered in widely separated portions of the book could have been largely compensated for by more frequent cross-references and by the numbering of paragraphs.

Considering the emphasis placed on the most modern aspects of physical theory, it is surprising to find so much attention paid to Maxwell's views concerning the nature of k, μ and the ether. Considerable space is devoted to magnetism and magnetic properties of iron; but the atomic theory of magnetism is far from modern. Dielectric phenomena are inadequately treated, and the word "electrostatics" is not found in the index.

The author's care in calling attention at various points to discrepancies between theoretical formulas and actual practice is greatly to be commended, as is also the frequent application of physical principles to everyday phenomena. On the other hand, in some instances not enough attention is paid to pointing out limiting conditions, as on pages 520 to 524, on water waves, where insufficient emphasis is laid on the effects of depth of water and of surface tension; or on page 531, where the significance of the two specific heats in their influence on the velocity of compressional waves in a gas is barely mentioned. The interpretation of tables and diagrams is not always obvious nor clearly explained, as for example on pages 569, 578, and 583.

Among the most excellent chapters may be mentioned those on the energetics of fluids, interference, diffraction and polarization of light, and radioactivity. The illustrations are particularly well executed.

W. G. CADY

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE MINNEAPOLIS MEETING, NOVEMBER 30 AND DECEMBER 1, 1928.

The 153rd regular meeting of the American Physical Society was held in Minneapolis, Minnesota, at the new Physics Laboratory of the University of Minnesota on Friday and Saturday, November 30 and December 1, 1928. The presiding officer was Professor Karl T. Compton, president of the Society. The special feature of the meeting was the formal dedication of the new Physics Laboratory of the University.

On Friday afternoon there was held a Dedicatory Symposium. Professor Hermann Weyl of Princeton University delivered an address: "*Laws of Conservation and Rules of Intensity in Quantum Mechanics.*" This address was followed by four papers on electron impact phenomena: "*Scattering of Electrons*" by Professor K. T. Compton of Princeton University; "*Quantum Theory of Aperiodic Effects*" by Professor E. U. Condon of Princeton University and Dr. J. R. Oppenheimer; "*Photo-ionization and Recombination*" by Dr. F. L. Mohler of the Bureau of Standards; and "*Motions of Positive Ions in Ionized Gases*" by Dr. Irving Langmuir and Dr. Lewi Tonks of the General Electric Company.

On Friday evening the members of the Physical Society were the guests of the University at a dinner held in the ballroom of the Minnesota Union. Following this dinner the Dedicatory Exercises were held in the Physics Auditorium. Professor John Zeleny delivered the dedicatory address "*The Place of Physics in the Modern World.*"

At the regular meeting of the Council held on Friday, November 30, 1928, two were transferred from membership to fellowship and one hundred and seventy-one were elected to membership. *Transferred from Membership to Fellowship:* Francis A. Jenkins and W. W. Stifler. *Elected to Membership:* Milton L. Almquist, Owen W. Anderson, Howard L. Andrews, Donald C. Archibald, Edward G. F. Arnott, Arnold E. Baragar, Frank A. Barta, Ernest Basch, C. A. Beck, Paul Bender, William Bender, James L. Bennett, Charles E. Berger, Carl V. Bertsch, K. Charlton Black, Edward M. Boardman, Langford T. Bourland, Walter H. Brattain, Herbert J. Brennen, Cecil W. Byers, William A. Calder, Robert J. Cashman, Cyrus L. Clark, T. R. D. Collins, DeVer Colson, F. W. Cooke, Paul L. Copeland, Allen W. Coven, F. W. Crawford, S. A. Deel, Walter H. Dehlinger, W. Edwards Deming, David M. Dennison, Francis G. de Quevedo, Jane M. Dewey, E. G. Dick, Ellis H. Dixon, Dorothy M. Dodd, Arpad E. Elo, Edgar W. Engle, Harry

Engwicht, H. D. Fagan, J. E. Field, C. W. Foard, J. H. Frazer, Carl A. Frische, George W. Gardiner, Jr., Paul H. Garrett, Irving G. Geib, Justin L. Glathart, Paul R. Gleason, Norris W. Goldsmith, Frank H. Graham, E. H. Greibach, Daniel T. Gundersen, Ross Gunn, A. N. Guthrie, Clinton R. Hanna, N. A. Haskell, Glenn G. Havens, L. J. Haworth, Lewis G. Headrick, Allan Hemingway, Malcolm C. Henderson, Dugald Hepburn, William B. Hogg, Carl E. Howe, Joseph H. Howey, Albert G. Hoyem, Paul Huber, C. E. Ireland, R. N. Jones, G. B. Karelitz, J. M. B. Kellogg, W. J. Kimmel, E. Lee Kinsey, Harry V. Knorr, Serge A. Korff, H. A. Kramers, Walter Krausnick, Zing Whai Ku, Franz D. Kurie, Frederick R. Lack, Floyd L. Leidal, Fred B. Llewellyn, Julian E. Mack, John A. Madigan, Kenneth V. Manning, R. C. Mason, Lorne A. Matheson, A. B. McLay, H. E. Mendenhall, Walter C. Michels, Allan C. G. Mitchell, Dana P. Mitchell, Thomas A. Mitchell, William R. Morgans, Melvin M. Morris, I. E. Mouromtseff, Ralph H. Müller, Frank E. Meyers, Seth H. Neddermeyer, Howard E. Nelson, H. R. Nelson, Kirsten L. Newbury, Robert F. Nicholson, Harold H. Nielsen, Charles M. Olmsted, Paul J. Ovrebo, James S. Owens, Louis A. Pardue, Sheldon J. Peirce, Jacob C. Peters, Charles W. Philpott, H. G. Pickett, Grant L. Pistorius, Boris Podolsky, Thomas C. Poulter, J. Harris Purks, Robert H. Randall, Aldo A. Ratti, Joseph Razek, Rufus K. Reber, Herbert J. Reich, Lloyd H. Reyerson, Lorenco A. Richards, Bernhard E. Richert, Oliver A. Riddel, Oscar L. Roberts, John M. Robertson, H. W. Rollmann, Walter W. Romig, John E. Ruedy, Audrey Ryan, D. C. Sheldon, W. Lewis Shetler, Joseph J. Shonka, David Sinclair, Burke Smith, Benjamin L. Snavely, Adolf Soroos, Ross D. Spangler, Luville T. Steadman, Paul J. Steele, Ralph R. Stevens, E. C. Stevenson, Donald C. Stockbarger, J. A. Stratton, Jabez C. Street, John Strong, Hugo N. Swenson, James A. Swindler, Albert C. Thompson, Clifford L. Treleaven, Edward M. Thorndike, George E. Uhlenbeck, Lal C. Verman, Francis E. Washer, Tully Watson, Alexander Weinstein, William Wertzbaugher, Martin D. Whitaker, Hassler Whitney, Hugh H. Willis, Earl D. Wilson, Ralph P. Winch, Robert M. Woods, Carl S. Woodward, Norman Wright, Henry L. Yeagley, Harold A. Zahl.

The regular scientific session consisted of forty-six papers (eleven of which were read by title), abstracts of which are given on the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB, *Secretary*

ABSTRACTS

1. Surface friction in tubes not of circular cross section. S. R. PARSONS, University of Arkansas.—The equations for frictional resistance to turbulent passage of a fluid through a tube of circular cross section have been adapted for use with tubes of other forms of section, by the use of expressions involving hydraulic radius rather than diameter. Schiller has shown (Zeits. Math. u. Mechanik, 3, 2, (1923)) that the method is applicable to a number of forms, including, square, rectangular, and triangular; and Davies and White (Roy. Soc. Proc., A 119, 92, (1928)) have extended it to pipes of very narrow rectangular section. Computations based on Lonsdale's experiments with water flowing through the annular space between two coaxial

cylinders (Phil. Mag. **46**, 163, (1923)) show that the method is applicable also to this case. Further computation shows that the equation of Lees for surface friction in circular tubes (Roy. Soc. Proc. **A91**, 46, (1914)) may be adapted to each case mentioned above, by substituting four times the hydraulic radius for the diameter of the tube. (This hydraulic radius is defined as the ratio of the area of cross section to the total perimeter, which is one half as great as the value used by Schiller.)

2. Entropy and probability. W. S. KIMBALL, Michigan State College.—The subject is treated by a new method distinct from (a) the kinetic method and (b) the statistical method. The procedure is characterized by elementary probability methods without reference to collisions or molecular ensembles in phase space. The probability of the state of each molecule is calculated separately and the product for all molecules gives the probability of the state of the gas. Six axioms are laid down: The probability of a particle's occupying a position in ordinary space equals the probability of its occupying any other position in ordinary space. Likewise with velocity space, momentum space, orientation space, and angular momentum space. These five axioms are generalized into a single axiom that includes all the others: The probability of a particle's having a position in action space equals the probability of its having any other position in action space. These axioms are supported by the Relativity Principle, and Liouville's Theorem. On the other hand they disagree with the quantum theory, but may be modified so as to incorporate it by restricting a particle's position in action space to integral multiples of Plank's h. The key note of the procedure is to measure probability by the range in action space (of not more than six dimensions) that includes each molecule. The new expression for "weight" is equivalent physically though of different form from the usual one from statistical mechanics involving factorials. Maxwell's distribution law is shown to be most probable by this new method of derivation, and the known expressions for entropy and the chemical constants for different types of gas are obtained. Plank's "Zustandsumme" or summation state is shown to be the action range per molecule in its average energy state, divided by the quare root of e, once for each degree of freedom.

3. Measurement of the intensity of high frequency magnetic fields. ROY H. MORTIMORE, State University of Iowa.—A method was developed for the measurement of the intensity of magnetic fields in the range of wave-lengths from 12 to 30 meters. Two methods were employed. By the first method the current in a circuit was computed from vacuum tube voltmeter readings of potential drop across a standard inductance. The values for current thus obtained were compared with the readings of thermo-ammeters in the range for which they were calibrated. For larger currents the instruments were shunted and calibrated for particular wave-lengths by the standard inductance method. The instruments thus calibrated were used to measure the currents in a Helmholtz coil and from these measurements the field intensities within the space enclosed by the coil were computed. By the second method the electromotive force induced in a single turn coil placed in the field to be measured was indicated by a vacuum tube voltmeter. The field necessary to induce the observed electromotive force was computed. Good agreement was found between the results obtained by the two methods.

4. A direct-current amplifier for measuring very small currents. J. M. EGLIN, Bell Telephone Laboratories, Inc.—A direct-current amplifier consisting essentially of a Wheatstone bridge, having the amplifying tube in one arm and a balancing tube in another, was recently described by Wynn-Williams (Proc. Camb. Phil. Soc. **23**, 810, (1927)). This has been developed to give a constant amplifications for currents in either direction up to 10,000 times the lowest measurable value. The amplification and the lowest measurable current are alterable together by changing the resistance introduced between the grid and filament of the amplifying tube. With tubes of high insulation, the amplification can be made as large as 10^4; and the measurable current as low as 10^{-14} ampere. Some improvements of the circuit are: (1) the insertion of a resistance in series with the tube in one arm of the bridge to "compensate" for variations in plate and grid battery voltages; (2) the suspension of the tubes to protect

them from mechanical vibrations; (3) the use of tubes with pure tungsten filaments, to avoid changes in contact potentials, and with plates enclosing the filaments completely, to lower the effects of wall charges. In a "null" method of using the circuit, the values of the grid resistance and an auxiliary potential introduced in the grid-filament circuit are sufficient to determine the measured current.

5. Amplification of photoelectric currents. HAROLD A. WHEELER, Johns Hopkins University.—A convenient and rugged amplifying apparatus has been developed for the direct measurement of very small photoelectric currents (or x-ray ionization currents). The light beam is interrupted by a rotating sector wheel at a frequency of 150 cycles per second; the resulting 150-cycle alternating component of the photoelectric current is amplified more than 10^6 times by a three-stage, broadly resonant, vacuum tube amplifier; the amplified current is rectified by a synchronous commutator with adjustable brushes; and the rectified current is measured by a portable micro-ammeter whose deflection is directly proportional to the photoelectric current. The factor of proportionality is determined by introducing a known current into the photoelectric cell circuit from a second set of brushes on the same commutator. The only time lag in this measurement is the period of the microammeter, about two seconds. The accuracy of measurement of very weak currents is limited by fluctuation phenomena in the amplifier. In selectivity against fluctuations and other disturbances, this system is equivalent to a sharply resonant amplifier with a resonance curve only one-half cycle in width. In the experiments performed, the fluctuations caused a "probable error" of between 10^{-14} and 10^{-13} ampere (for a single observation). Improvements have been outlined which should reduce this error to below 10^{-15} ampere.

6. Excitation of band spectra. JOSEPH KAPLAN AND E. L. KINSEY, University of California at Los Angeles.—The β bands of nitric oxide are only weakly excited in electric discharges and strongly excited in active nitrogen. Their excitation in active nitrogen is by collisions of the second kind, while in discharge tubes it is due to electron impact. This difference in the excitation of spectra by electron impact and by collisions of the second kind can be explained by means of the Franck-Condon curves for the two levels that are involved in the transition. The most probable transition for electron impact is one in which the vibrational motion in the upper level is determined by the instantaneous values of the separation of the atoms r and their relative momentum p_r. The difference in binding between the upper and lower states of the β bands is very large and explains the non-excitation of the known bands. Their excitation by collisions of the second kind is interpreted as meaning that the energy transfer during a collision of the second kind requires a time so long that the transfer does alter the instantaneous values of r and p_r. It is therefore possible to make diagonal jumps between two Franck-Condon curves, by collisions of the second kind.

7. New bands in the secondary spectrum of hydrogen. G. S. MONK AND A. E. ELO, University of Chicago.—Using the electronic and vibrational levels associated with the Balmer lines, which have been obtained by Richardson, the wave-numbers of the remaining lines of the band groups have been computed, and compared with measured lines in the tables of Gale, Monk, and Lee, and of Poettker. Only Q branches are found, a fact in agreement with the work of Richardson, whose results for the P and R branches are fragmentary. The absence of the P and R branches in the present work is probably attributable to the faintness of the new bands, only the Q branches being strong enough for observation. The reality of the branches thus found depends in part on the accuracy of Richardson's data, which are better for the α, β, and γ electron levels than for higher levels. Some bands attributable to the H_3 molecule have been found in the new measurements of Gale, Monk, and Lee, and of Poettker. The evidence for the reality of these bands is discussed.

8. The band spectrum of fluorine. H. G. GALE AND G. S. MONK, University of Chicago.—New Measurements show the bands of this spectrum to consist of P, Q, and R branches with alternate weak and strong lines in each branch. The Q branch is about twice as strong as the P or R branch. Two of the strongest bands whose initial points lie at $\nu = 16378.8$ and $\nu =$

17439.5 have been completely analyzed and three fainter bands at $\nu=15337.6$, $\nu=17075.0$, and $\nu=18550.0$ partly analyzed. There are strong perturbations in all the bands in both frequency and intensity, which have heretofore masked their true character. These perturbations are in the initial state, with a single perturbation probably belonging to the final state. The following values have been obtained:

$B_0'=0.840$, $B_0''=1.095$, $I_0'=32.9\times10^{-40}$, $I_0''=25.3\times10^{-40}$, $\omega_0'=847$, $\omega_0''=1132$, $\alpha=0.015$.

The structure and intensity relations indicate that the bands are of the $'S\rightarrow'P$ type. Neglecting strongly perturbed intensities, the best plates show the ratio of intensity of weak to strong lines to be about 1:3, indicating that the fluorine atom possesses a nuclear spin of one-half (in quantum units).

9. The metastable states of atomic nitrogen. K. T. COMPTON AND J. C. BOYCE, Princeton University.—A study of the extreme ultra-violet spectrum of nitrogen excited by controlled electron impacts, together with a consideration of the spectra obtained by Hopfield, Fowler, and Millikan and Bowen, has enabled us to extend the analysis of near-visible lines made by Kiess so as to give practically the entire spectral structure predicted by the Hund theory. The "ground" state $2p^4S$ has a term value of about 117345, as found by Hopfield. The two next lowest states are $2p^3D_{2,3}$ and $2p^3P_{1,2}$ at about 98143 and 88537 respectively. These states are metastable. The separation of the D terms is about 5, and that of the P terms probably not more than 1. *Active nitrogen.* The energies of these states are 2.37 and 3.56 volts, respectively. These are just the energies of the entities in active nitrogen which Kaplan and Cario, working in this laboratory, found necessary to account for production of the "afterglow" by excitation of the ^3S metastable molecules, and for excitation of other spectra in "dark" active nitrogen. There seems, therefore, to be no doubt that the two types of metastable atoms and the metastable molecule are singly or jointly responsible for the varied phenomena of active nitrogen.

10. The diffraction of light by a circular opening and the Lommel wave theory. MASON E. HUFFORD AND HAROLD T. DAVIS, Indiana University.—In a paper published by E. Lommel in 1886 the conditions for a maximum or minimum of light intensity in a diffraction pattern produced by light passing through a circular opening are derived. The equation for maxima and minima involves the Bessel functions and the Lommel U-functions. These equations and the Lommel theory have not been verified except for very small diffraction patterns produced by light through comparatively small distances. Some experiments in which very large diffraction patterns were produced by light passing through comparatively large distances offered an opportunity to verify the theory through a much larger range. Professor H. T. Davis has contributed new equations for calculating the Lommel U-functions involved in calculating the intensity of light at 256 points along a radius in the pattern. Graphs of the intenisty in the pattern have been made. From these at points representing maxima and minima numerical values were taken for substituting in the Lommel equations for calculating the radii of the diffraction rings. These calculated radii have been compared with radii measured on the diffraction patterns.

11. Combination scattering in liquids. R. M. LANGER, National Research Fellow, and W. F. MEGGERS, Bureau of Standards.—The scattered light of modified wave-length predicted by quantum theory and recently found experimentally by Raman and Krishnan differs from the incident by a frequency equal to an absorption frequency of the scattering substance. This frequency shift produces a wave-length shift which increases with the wave-length of the scattering line. It would then be desirable for accurate measurement to use as long an exciting wave-length as possible. Prism spectrographs which, because of their light gathering power, have been used exclusively hitherto have very poor dispersion in the visible. In the ultra-violet their increased dispersion and the relative increase in intensity of modified lines are offset by the decreased wave-length shift and especially by the chemical action of the incident light on the scattering substance which often gives a great deal of trouble. Moreover many interesting substances are opaque in the ultra-violet. We have, therefore tried for

the effect with a 21 ft. concave grating and have succeeded in getting good plates in 1 to 2 hours exposure. Under this high dispersion the modified lines vary in character, some being complex, some hazy, some unsymmetrically shading off to the violet. What is more surprising is that others, for example the ones in benzene corresponding to a shift of 992 wave-numbers, are comparable in sharpness with the exciting Hg lines and the wave-lengths of such lines are measurable with an accuracy of one or two hundredths Angstrom unit.

12. Temperature variations of the Raman effect in quartz. F. G. BRICKWEDDE AND M. F. PETERS, Bureau of Standards.—Photographs were obtained of the Raman effect in crystalline quartz over a range of wave-lengths from 2400 to 5000A and of temperatures from $-180°$ to 550°C. The intensity of the anti-Stokes lines corresponding with the 21μ absorption band increase greatly with rising temperatures. Stokes lines change only slightly with temperature, the line accompanying 2536 decreasing slightly with rising temperature. The anti-Stokes lines corresponding with an 81μ band increase less rapidly than do those corresponding with 21μ band. The corresponding Stokes line decreases in intensity. These results are in qualitative agreement with the assumption that intensities of Raman lines vary as the populations of the initial states which give rise to them, the population of the states varying with temperature in accordance with Boltzmann's law. Displacements from the exciting line of Raman lines corresponding with 21μ and 81μ bands decrease with rising temperatures. This is expected if these infra-red bands move to longer wave-lengths. With rising temperature Stokes lines corresponding with the 21μ band—sharp at room temperature—become diffuse, and anti-Stokes lines—diffuse at room temperature—become broader and more diffuse. The intensity of the Raman scattering increases markedly in passing from longer to shorter wave-lengths of incident light.

13. The scattering of light by electrons. GEO. GLOCKLER, University of Minnesota.—On the principle of microscopic reversibility Klein and Rosseland (Zeits. f. Physik. **4**, 46, (1921)) deduced the possibility of impacts of the second kind. Writing the reaction as a chemical equation, it is seen that the reverse reaction always represents the impact of the second kind. For example Hg $(1'S)+h\nu$ (2537A)$\rightleftarrows$Hg(2^3P_1) absorption and emission; M(normal$+h\nu\rightleftarrows$M(excited$+h\nu'$, Raman effect: $h\nu+E^-$(slow)$\rightleftarrows h\nu'+E^-$(fast), Compton effect, where $h\nu'$ is the scattered quantum and E^-(fast) is the resulting photoelectron. On the principle stated above it is possible to predict the inverse effect, the scattering of light by fast electrons. The equations for head-on collision between a quantum and a free fast electron showing the change the wave-length is

$$\Delta\lambda=[(2h)/(mc)\pm 2\lambda_1\beta]\cdot[(1\pm\beta)\ (1\mp\beta)]^{1/2}$$

For a large quantum (x-rays) and a slow electron this reduces to Compton's equation. For visible light the ordinary Compton effect would be very small. However, the interaction of visible light with fast electrons should modify the quantum. The green line of mercury 5461A° should show a change of 685A when interacting with a 1000 volt electron in a head-on collision. The demonstration of this effect experimentally would depend upon the possibility of obtaining a powerful source of radiation and a dense electron-stream. In an arc or other source of radiation the above effect may be the cause of continuous spectra.

14. The effect of external fields on the polarization of the light in hydrogen canal rays. I. WALERSTEIN, University of Toronto. (Introduced by A. J. Dempster.)—By means of a specially constructed aluminum cathode having a canal 6 mm long, it was possible to observe the light radiated by moving hydrogen particles before entering the canal, then in the canal itself, and finally in a high vacuum chamber beyond the canal in which the intensity of the light falls off exponentially. The effects on the polarization of the light was observed when electric and magnetic fields were applied in different directions. For weak magnetic fields applied perpendicular to the canal ray there is a decrease in the polarization of the light in the canal. In the high vacuum chamber the polarization ordinarily falls to zero a short distance from the canal end, but on applying magnetic fields this decay of the polarization is disturbed and fluctuations in the polarization occur which are nearly periodic along the canal ray. The

periods increase with higher fields. The initial effect of the field begins closer to the canal end as the field is increased, there is a difference in the effect produced depending on whether the field is parallel or perpendicular to the direction of observation. Similar changes in the polarization were also obtained when electric fields varying from 50 volts to 1200 volts were applied either along the canal ray or perpendicular to it.

15. Electrodeless ring discharge and the production of atomic rays of hydrogen. JACOB KUNZ and J. T. TYKOCINER, University of Illinois.—For the determination of the magnetic moment of the hydrogen atom a new method of production of atomic rays and a new slit system has been tested. The method consisted in inducing high frequency discharges in an electrodeless quartz bulb supplied with H_2. The bulb was connected to a quartz tube containing the slit system. The latter was made of semicircular quartz plates 1 mm thick, ground along the slit-forming edges to 0.03 mm, aligned and sealed at the ends of the quartz tube by special auxiliary apparatus. A thin platinum foil of 0.02 mm thickness, introduced between every pair of the semicircular quartz plates and then dissolved, left open well defined slits. The pressure of 2×10^{-4} mm was maintained in the slit system. A fine line of 0.05 mm thickness was obtained on the screen while the a.c. electromagnet was left unexcited. Remarkable, however, was the observation that whenever the magnetic field was applied the ring discharge was suddenly interrupted. Magnetic shielding of the discharge bulb and reduction of the magnetizing current from 8.5 to 3 amperes was required. A clean and sharp separation of the original line into two lines was then obtained.

16. The positive-ray analysis of hydrogen sulphide. JAMES H. BARTLETT, JR., Harvard University.—In the study of hydrogen sulphide by Dempster's method of positive-ray analysis, three principal types of ion were found, namely $(H_2S)^+$, $(HS)^+$, and $(S)^+$, with ionization potentials of 11.1 ± 1.5 volts, 17.6 ± 1.5 volts, and 16.5 ± 1.5 volts, respectively. If the voltage scale be calibrated by assuming the correctness of Mackay's determination of the lowest ionizing potential of hydrogen sulphide as 10.4 volts, then the corrected values of the ionizing potentials are approximately 10.4, 16.9, and 15.8 volts respectively. Neither $(S_2)^+$ ions, nor hydrogen ions, nor negative ions were observed. Variation of the pressure, at low pressures, shows that no secondary processes occur, i.e. that the ions $(H_2S)^+$, $(HS)^+$, and $(S)^+$ are all formed by the initial process of the electrons colliding with the gas molecules.

17. Measurement of the life of the metastable mercury atom. M. L. POOL, Ohio State University.—A high speed disk has been used to interrupt the total radiation from a water-cooled and magnetically controlled quartz mercury arc that excited resonance radiation in mercury vapor contained in a quartz resonance tube at room temperature. Approximately 10^{-4} sec. after the optical excitation, a flash of visible radiation from another mercury arc was passed through the resonance tube and the absorption spectrum photographed. The line 4047 ($2^3P_0-2^3S_1$) showed strong absorption when a few millimeters of nitrogen were introduced into the resonance tube. The lines 4077, 4358, 5461, 5770 and 5790 showed no measurable absorption under similar conditions. The rate of decrease of the amount of 4047 absorbed with increasing time-wait after excitation of the mercury vapor was taken as the rate of decay of the metastable 2^3P_0 state. The life or half-value time of the state was found to vary markedly with the pressure of the admixed nitrogen. The maximum life, 4.2×10^{-4} sec., occurred for 6.8 mm of nitrogen. No absorption of 4047 was observed upon the introduction of hydrogen, argon, neon or helium into the resonance tube.

18. Inelastic collisions of electrons with mercury atoms. JOHN D. WHITNEY, State Teachers College, Oshkosh, Wisconsin.—A beam of electrons is taken from a region containing Hg vapor into a highly evacuated space and is there spread out into a "velocity spectrum" by means of a magnetic field. The intensity of each component of the spectrum is measured for various initial energies of the electrons up to 40 volts. The ratio of the number of inelastic collisions of a given type at a given voltage to the number of elastic collisions at that same voltage is plotted against the initial energy of the electrons for the 4.9-, 6.7- and 8.8-volt types of collisions. Each curve shows a well-defined maximum in the range studied. For the 4.9-volt

type it is at 7 volts; for the 6.7-volt type at 15 volts; for the 8.8-volt type at 12 volts. The heights of the maxima decrease in the order named. No evidence is found for collisions involving a loss of 10.4 volts.

19. Shot effect in thermionic emission from oxide coated electrodes. N. H. WILLIAMS AND W. S. HUXFORD, University of Michigan.—Recent investigations in this laboratory have resulted in the successful determination of the charge of positive thermions from measurements of shot effect. A special type of hot electrode made of barium oxide has been found to emit positive ions as well as electrons. The conditions are quite the reverse of those resulting in the case of positive ion emission from potassium-iron oxide crystals; in the latter the electron emission is very small in comparison to the ion emission, for low temperatures. Measurements of the ionic charge yield a value equal in magnitude to the charge of the electron, and the results are analogous to those obtained for K^+ ions from iron oxide crystals. In the present case space charge conditions are modified by the presence of large numbers of emitted electrons. Results of electron charge determinations are similar to those obtained with oxide coated filaments by J. B. Johnson. In the present study, however, the analysis is carried much farther and the limiting conditions obtained for a random electron distribution in the emission.

20. The effect of H_2O on the final positive air ion. HENRY A. ERIKSON, University of Minnesota.—The positive ion is produced in air or nitrogen which has been passed through calcuim chloride and phosphorous pentoxide at a rate sufficiently slow to reduce the amount of H_2O to a neglibile quantity. The initial positive ions are allowed to age until only the final 1.36 positive ions remain. H_2O is then added and the positive ions allowed to remain in the moist air for different intervals. It is found that the initial 1.87 ions again appear and the number of final 1.36 ions is diminished. As the time is increased more of the initial ions are obtained until a maximum is reached when the number of initial ions diminishes until only the final 1.36 ions are left. The number of final 1.36 ion during the above ageing dimishes to a minimum, and then increases again in number. The minimum corresponds in time to the maximum for the initial ion. The explanation apparently is that the neutral H_2O molecule gives up an electron to the final 1.36 two molecule air ion thus forming a positive one molecule 1.87 H_2O ion which in turn attaches itself to a neutral molecule forming again a final 1.36 two molecule ion.

21. A test of the state of polarization of reflected electron waves. C. J. DAVISSON AND L. H. GERMER, Bell Telephone Laboratories, Inc.—An electron beam strikes a $\{111\}$-face of a nickel crystal at 45°. The reflected beam strikes a second similar crystal at the same incident angle. A Faraday collector receives those electrons which are reflected from the second crystal without loss of energy. The collector and second crystal are rigidly joined and and rotate about the axis of the beam proceeding from the first to the second crystal. Measurements upon the doubly reflected beam have been made at bombarding potentials from 10 to 150 volts. This beam exhibits five intensity maxima, at 20, 55, 77, 103 and 120 volts. Three of these maxima were observed in our reflection experiments (Proc. Nat. Acad. **14**, 624 (1928)—Fig. 3). The other two were outside the range of these experiments. Polarization of the electron waves reflected from the first crystal would manifest itself by a doubly periodic variation of collector current when the collector and second crystal are rotated. We observe no such variation. If it exists its amplitude is less than two percent of the total current, and in the case of the strong 120 volt beam is less than one percent. According to our observations electron waves are not polarized by reflection.

22. Velocity of cadmium atoms specularly reflected from rock-salt crystals. A. ELLETT AND H. F. OLSON, University of Iowa.—Using a rotating sectored disc velocity analyzer we find that the beam of cadmium atoms specularly reflected from a clean rock-salt crystal is composed of atoms having all very nearly the same velocity. This velocity varies with the angle of incidence, but not with the temperature of the crystal. The results may be represented by the equation

$$\lambda = h/M_H v = 2d\{\mu^2 - \mathrm{Sin}^2\theta\}^{1/2}$$

Here M_H is the mass of the proton, $\mu = 1.5$ the "index of refraction for phase waves." This equation may be interpreted in terms of deBroglie's ideas by assuming that the periodicity associated with an atom is merely that characteristic of the protons which compose it. A similar result for the wave-length associated with the translation of a system of Z particles of equal mass may be obtained from Schroedinger's equation if the kinetic and potential energies both contain Z as a factor.

23. The resistance of mercury arcs. ALBERT W. HULL, General Electric Co.—The volt-ampere characteristic of a constant-pressure mercury arc is negative for small currents, nearly zero for moderate currents, and steeply positive for large currents. The positive portion has received very little attention. It has been described by Langmuir and Mott-Smith (G. E. Review, **27**, 770, (1924)) for the case of a discharge through a quartz capillary; but it does not appear to be known that this positive resistance is a general characteristic of low pressure arcs, occurring, for example, in the largest mercury arc rectifiers under operating conditions. Calculations of positive ion density by the method of Langmuir and Mott-Smith show that the positive resistance is always associated with the approach to complete ionization of the gas. The positive resistance is thus a normal characteristic of low pressure arcs, due to the increased energy per unit current necessary to maintain the discharge when the fraction of atoms ionized becomes appreciable. Further evidence is furnished by the fact that two such arcs may be operated in multiple without stabilizing resistance or reactance, and share the current equally when the total current is sufficient to bring them into the positive resistance range.

24. The duration of the effect of ions on a negative space charge. C. BOECKNER AND F. L. MOHLER, Bureau of Standards.—A two electrode tube containing caesium vapor was operated under conditions described by Foote and Mohler (Phys. Rev. **26**, 195 (1925)) for detection of photo-ionization by the space charge effect of positive ions. Photographic records were obtained with a string galvanometer of the current rise and decay upon admitting and shutting off light. The effect requires one or two seconds to decay. The time-current curves follow the equations $d\Delta/dt = -\alpha I\Delta$ for decay and $d\Delta/dt = \alpha(I_f\Delta_f - I\Delta)$ for the rise. I is the current at time t, I_f the final current after illumination while Δ and Δ_f are the differences between these currents and the dark current. α is a constant independent of the amount and place of illumination, of the voltage and current. It changes slowly with pressure and increases with filament area. An electric surge in a neighboring circuit produces a current which decays exactly like the photo-electric effect. Assuming that Δ measures the number of ions and therefore: $\alpha I\Delta$ their rate of dissappearance, then at equilibrium the light intensity must be proportional to $I\Delta$. Whitman has found this relation to hold (unpublished). The imprisonment of the ions in the potential minimum known to exist about a filament at low voltage may explain the long life.

25. The photographic activity of cod liver oil. JAY W. WOODROW, Iowa State College.—In the experiments described in this brief report it has been shown that the oxidation of cod liver oil is accompanied by the emission of particles which are capable of producing a developable image on a photographic plate. These particles experience only a small amount of scattering in passing through thin sheets of cellophane and are only slightly deflected by a stream of air. The shadows which are produced by objects placed several millimeters from the photographic plate with a sheet of cellophane placed between the object and the sensitive film, are much sharper than one would expect if it were a case of simple diffusion. The particles are completely absorbed by a few centimeters of air. The absorption in cellophane obeys the ordinary exponential law, the coefficient of absorption being about 150 per cm. The effect is very much increased by a rise in temperature.

26. Becquerel effect in cells containing Grignard compounds. R. T. DUFFORD, University of Missouri.—Observations were made on nearly 100 cells containing anhydrous ether solutions of Grignard reagents (organo-magnesium halides), with various metals as electrodes. Such cells polarize readily, and show voltage drift, reversal, and oscillations, similar to effects shown to exist in aqueous solutions. The voltage of such cells is markedly sensitive to light, apparently to the longer visible wave-lengths. Some cells show an increase, some a decrease,

of voltage on illumination. Temperature effects appear much too small to explain the observed changes, and are usually in the opposite direction. Each solution shows an optimum concentration for photo-sensitivity, this concentration being higher for aromatic than for aliphatic compounds. Results from eleven typical solutions indicate that the photo-sensitivity is most pronounced with the compounds that give the brightest luminescence on oxidation with oxygen. This work was done at the Research Laboratory, Incandescent Lamp Works of General Electric Co., Nela Park, Cleveland, Ohio.

27. The M-series x-ray absorption spectra of metallic platinum and gold. ARTHUR J. M. JOHNSON, State University of Iowa.—The M-absorption spectra of metallic platinum (78) gold (79) have been investigated by the use of a vacuum spectrograph. Five discontinuities were found for platinum at wave-lengths of 5.711A (M_1), 5.506A (M_2), 4.677A (M_3), 4.085A (M_4), and 3.742A (M_5). For gold only four were found at 5.506A (M_1), 5.315A (M_2), 4.501A (M_3), and 3.603A (M_4). The $(\nu/R)^{1/2}$ values for the experimentally determined wave-lengths of these discontinuities compare well with the values predicted by the use of absorption and emission data from the L-series except for the M_1 and M_2 levels. For these two levels the measured wave-length values are unmistakably less than the computed values. This displacement of these two discontinuities for both of the elements investigated is in agreement with the results of others, (Zumstein, Phys. Rev. **25,** 747 (1925), and Rogers, Phys. Rev. **30,** 747 (1927)), upon neighboring elements of high atomic weight in which compounds of the elements were used in the absorption screens. The possibility of the displacement of these discontinuities being due to "chemical effect" is very remote. Since apparently the data from which the positions of the M-discontinuities are predicted are of more than sufficient accuracy to justify confidence in computations made with their use, it seems that the simple application of the combination principle in the prediction of these levels is not fully satisfactory.

28. X-ray anomalous dispersion in the region of the L-series of platinum. ELMER DERSHEM University of California.—The indices of refraction of platinum in the neighborhood of its L absorption limits were measured by the total reflection method. When values of $1-\mu=\delta$ are plotted against the corresponding values of λ one depression in the curve shows lowered values of δ at a wave-length corresponding to a mean of the wave-lengths of the L_{I} and L_{II} limits and another at the L_{III} limit. Evidently the L_{I} and the L_{II} limits are not resolved because of relatively small wave-length separation, whereas in the case of silver (Phys. Rev. **31,** 1117, (1928)) the L_{II} and L_{III} were not resolved. In the latter metal these levels are closer together than L_{I} and L_{II}. Using a platinum film nearly opaque to light, values of δ in fair agreement with theory were obtained. A thinner film, estimated as transmitting at least 80 percent of visible light, gave a curve whose δ values were at all points about 25 percent higher than for the nearly opaque film. Other experiments are cited which show that different surfaces of the same material may have very different indices of refraction.

29. Wave-length measurement of γ-rays from radium and its products. L. T. STEADMAN, Yale University. (Introduced by A. F. Kovarik.)—The work of Kovarik in this field has been continued using the method of crystal diffraction. γ rays from a 5 mg Ra source are limited by a slit of 3 mm width between two lead blocks 7 cm in thickness and incident on a crystal of calcite fixed in position at 20 cm. Those rays which are diffracted on transmission come to a focus at 40 cm from the source and are detected by a Geiger counter employing an amplifier and loud speaker. Two lead blocks 15 cm in thickness are used to form a slit 0.3 mm wide in front of the chamber and may be rotated about the focus as an axis, the angle being read to 7 sec. of arc. Results in good agreement with the previous workers, Rutherford-Andrade, Kovarik, Ellis-Skinner, and Frilley have been found. The following are some of the lines measured in X.U. $68\cdot 1^2$, $34\cdot 1$, $25\cdot 9$, $38\cdot 9^2$, $27\cdot 9$, $23\cdot 9$, $21\cdot 1^2$, $19\cdot 7$, $17\cdot 6^2$, $16\cdot 2$, $12\cdot 3$, $10\cdot 6$, $5\cdot 3$. (^{2} probably second order). There are other lines in evidence of intermediate and also of shorter wave-length. These will be measured and all repeated with greater accuracy.

30. The space group and crystal structure of potassium sulphate. FRANK PEAT GOEDER, University of Chicago. (Introduced by J. K. Morse.)—Crystals were grown by evaporation.

Sections cut parallel to the 100, 010 and 001 faces were mounted on perforated glass slides and a series of Laue photographs obtained. Analysis of these photographs placed potassium sulphate uniquely in space group $2Di$-13, (V_h^{13}). Powder photographs were then made using a General Electric apparatus. Analysis of these negatives gave the following values of the lattice constants, $a_0 = 5.771$, $b_0 = 10.064$, $c_0 = 7.518$A. The following positions gave the best agreement with all diffraction results

Potassium 000; 1/2 0 1/2; 0 1/2 1/2; 1/2 1/2 0; 0 0 1/2; 1/2 0 0; 0 1/2 0; 1/2 1/2 1/2
Sulphur 0 1/4 1/2; 1/2 1/4 0; 0 3/4 0; 1/2 3/4 1/2
Oxygen (.00, .15, .30); (.25, .35, .50); (.00, .15, .70); (.25, .35, .00); (.50, .15, .20); (.50; .15, .80); (.75, .35, .00); (.75, .35, .50); (.00, .65, .20); (.00, .65, .80); (.50, .65, .30); (.50, .65, .70); (.25, .85, .00); (.25, .85, .50); (.75, .85, .00); (.75, .85, .50).

A comparison between the relative intensities observed and those computed from the structure quantitatively verified this arrangement. Two points may be emphasized (1) the potassium sulphate molecule is clearly defined in the crystal and consists of a tetrahedral arrangement of the oxygen atoms having the sulphur at the center and the two potassium atoms on a straight line and equidistant from the sulphur atom; (2) while the potassium ions have the general positions of the space group, the sulphur atoms do not fit any special cases of the general arrangement.

31. The crystal structure of solid mercury. KARL LARK-HOROVITZ, Stanford University and Purdue University.—Applying the method used previously by the author in the investigation of the crystal structure of the alkali metals, (Phys. Rev. **29**, 352 (1927)) thin deposits of solid mercury were formed in a high vacuum and their crystal structure determined at different temperatures. The mercury was first condensed at liquid air temperature and sharp lines were obtained with copper and iron K radiation (in about 500 M.A. min.) confirming McKeehan's results. The mercury condensed at liquid air temperature was then brought up to the temperature of a carbon-dioxide-alcohol mixture and the crystal structure at this temperature was determined. It is found to be identical with the structure at lower temperature: the statement of former investigators that a different form of mercury exists at $-80°$C is therefore erroneous. Whereas the geometry of the lattice is identical, the lines are sharper at the higher temperature, and their relative intensity is sometimes changed, indicating an orientated growth of the crystals in warming up and re-crystallizing.

32. Diffraction of x-rays in liquids: benzene, cyclohexane and certain of the irderivatives. G. W. STEWART, University of Iowa.—An examination by the x-ray diffraction ionization method was made of benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, ethyl benzene and iso propyl benzene; cyclohexane, methyl cyclohexane, *o*-, *m*- and *p*-dimethyl cyclohexane; phenol, aniline, cyclohexanol and cyclohexanone. The cybotactic condition in the liquid and the applicability of Bragg's Law in determination of separation of diffraction centers, are assumed. Benzene and cyclohexane rings are shown to be distinctly flat, having a thickness of 4.70A and 5.10A, respectively. Assuming parallel hexagonal disks, the distance between two parallel sides of the hexagon is 6.0A in benzene and 6.4A in cyclohexane. These rings are so effectively flat that simple substitutions like OH and NH_2 with the benzene ring and O in the cyclohexane ring do not increase the thickness by a well defined amount. The substitution of a CH_3 group increases the thickness by 0.36A and 0.25A, respectively. In substituting two CH_3 groups in the ortho, meta and para positions, there is a striking similarity of the changes in the thickness of the ring, it being greater in the ortho position and least in the para position, the effect with benzene being the greatest. The two polar compounds, phenol and cyclohexanol, show the association of molecules, the polar end groups uniting with the molecules end to end and parallel to adjacent molecules, and lying in planes perpendicular to the planes containing the "disks." In *o*-xylene and mesitylene are shown a new and important "association of the second kind."

33. The effect of x-rays on the rotatory power of some substances. A. A BLESS University of Florida.—According to Allison, (Phys. Rev. **31**, 159, (1928)) x-rays falling on water and on some organic compounds affect the power of these substances to rotate the plane

of polarization of light passing through them. Experiments were made to discover a similar effect of x-rays on quartz crystals. A molybdenum water-cooled Coolidge tube operated at about 40,000 volts served as a source of x-rays. A half shadow type polarimeter on which readings could be made to 0.01 degrees was used. The quartz crystals ranged in thickness from 0.5 cm to 1.5 cm. No effect of x-rays on the rotation of the plane of polarization of light passing through these crystals was discovered. The error in "setting" was about 0.1 degrees. Experiments with water, sugar solutions and xylene failed to yield the positive results obtained by Allison. The error in setting for the organic solutions was about 0.6 degrees and for water, through which white light was allowed to pass instead of monochromatic as in the other cases, the error was less than 0.02 degrees. The tube containing the liquids was 22 cm long. The experimental work was done at Cornell University.

34. A mechanical analog to the hydrogen wave equation. J. H. VAN VLECK, University of Wisconsin.—This is only an elementary remark on how to visualize without mathematical analysis why positive energies are continuous, negative discrete. The hydrogen wave function is $\psi = S(\theta, \phi)f(r)$, where S is a tesseral harmonic and where, using the notation x, t rather than f, r, the equation for the radial factor is

$$\frac{d^2x}{dt^2} + \frac{2}{t}\frac{dx}{dt} + \frac{8\pi^2 m}{h^2}\left[W + \frac{a}{t} - \frac{b}{t^2}\right]x = 0.$$

This may be interpreted as the equation of an oscillator whose damping factor and restitution coefficient vary with the time. If $W>0$, this coefficient is positive for large values of t, and vibrations damp down to the equilibrium position $x=0$ at $t=\infty$ regardless of initial conditions. (Comparison with Bessel's Eq. shows the damping adequate despite the factor $2/t$.) Now there is always one solution finite at $t=0$, and from the preceding this solution will vanish properly at $t=\infty$ whenever $W>0$. Hence all positive W's are characteristic values. With $W<0$, the restitution coefficient is negative for large t, and consequently except under very special conditions the displacement x will tend to increase indefinitely as t approaches infinity. Thus it is plausible that only particular negative values of W make the solution which is finite at $t=0$ also finite at $t=\infty$.

35. Nuclear motions associated with electron transitions in diatomic molecules. Edw. U. CONDON, Princeton University.—The question of nuclear motions associated with electron transitions is discussed from the standpoint of quantum mechanics. It appears that Heisenberg's indetermination principle gives the clue to the inexactness of the earlier method (Phys. Rev. **28,** 1182, (1926)) based on Franck's postulate since its strict application calls for a violation of the principle. The existence of an entirely new type of band spectrum due to the wave nature of matter is predicted and the interpretation of Rayleigh's mercury band at 2476–2482A as of this type is suggested. Finally it is shown that while Franck's postulate is also true for electron jumps in atoms, it is of but trivial interest because its inexactness is much greater for the electrons than for heavy nuclei. The complete paper appears in the *Physical Review* for December, 1928.

36. Wave mechanics and radioactive disintegration. RONALD W. GURNEY AND EDW. U. CONDON, Princeton University.—Hitherto the "instability" of the radioactive nucleus has remained a mystery. But if the nuclear particles obey the laws of wave mechanics, the spontaneous disintegration of the nucleus by the emission of a particle may ensue. For by the wave mechanics particles are enabled to pass through regions in which their total energy would according to the classical mechanics be less than their potential energy. Thus a nuclear particle always has a certain probability of penetrating the barrier of potential which confines it, and of escaping from the nucleus. Any radioactive decay period from a fraction of a second to over 10^{10} years is easily obtained. For elements which expel α-particles we expect a relation between the rate of decay and the energy of the emitted particle of the same kind as that given by the Geiger-Nuttall relation. In favor of this theory of radioactivity there is the additional fact

that it predicts the well-known paradoxical result found by Rutherford and Chadwick for the scattering of fast α-particles fired at a film of uranium. A preliminary note by the authors on this subject appeared in *Nature* for Sept. 22nd.

37. On the separability of Schoedinger's equation for the asymmetrical top. S. C. WANG, National Research Fellow, University of Wisconsin.—By utilizing the results of Reiche on the problem of the asymmetrical top in the old quantum theory (Phys. Zeits., **19**, 394, (1918)), it is found that Schroedinger's equation for this problem is completely separable, when the spatial quantum number m is zero, in the set of coordinates introduced by Reiche. The two resulting ordinary differential equations, except for a difference in boundary conditions, are both of the form $(f(\lambda)^{1/2}d/d[(f(\lambda)^{1/2}d\ U/d\lambda]+(a+b)\ U=0$, where λ is one of the two elliptical coordinates λ_2 or λ_3 and $f(\lambda)$ a cubic, for the definition of all of which we refer to Reiche's original paper; and where U stands for $U_2(\lambda_2)$ or $U_3(\lambda_3)$ and a and b are two constants common to the two equations. The above equation resembles closely the generalized Lamé's equation investigated by Klein and Bôcher. A geometrical argument similar to the one used by Klein shows that there exist two sets of characteristic values for the constants a and b which specify admissible solutions in λ_2 and λ_3 respectively. Closed forms for the characteristic values and the characteristic functions have not yet been obtained.

38. Radiation by accelerated electron in classical electron theory. JOHN A. ELDRIDGE, University of Iowa.—It is considered fundamental in the classical electron theory that an accelerated electron must radiate energy. This appears to be contradicted by the older forms of the quantum theory. In the classical proof it is assumed that an electron charge surrounded by a static field is suddenly accelerated. Retarded potential solutions involving radiation of energy follow. But, it would seem that the initial conditions (of an accelerated charge in an undisturbed field!) are physically unrealizable. Whether or not radiation occurs appears to depend entirely upon the initial field conditions and those assumed in the usual theory are impossible.

39. Confirmatory experimental evidence of gas degeneration and the applicability of Pauli's exclusion principle to metallic conduction electrons. JESSE DU MOND, California Institute of Technology.—From the breadth and structure of the Compton shifted line the distribution of velocities of the scattering electrons can be inferred, the effect being similar to the Doppler broadening of optical lines. The structure of this line has been studied experimentally with a spectrograph contained in the x-ray tube for scattering by aluminum and beryllium at nearly 180° scattering angle. The results are compared with the line structure to be expected from the three following assumptions; first, that conduction electrons share classically in equipartition of the thermo-kinetic energy of the crystal; second, that they have the same velocities as they would have in the outer orbits of isolated atoms; third, that they are subject to the Pauli exclusion principle and have the velocity distribution predicted by Sommerfeld. The results are found to definitely support the third assumption.

40. The atomic electric charges in the electromagnetic quantum theory. CORNELIO L. SAGUI, Castelnuovo dei Sabbioni, Arezzo, Italy.—Gravity is supposed to be due to a magnetic depression between two bodies resulting from the reaction of opposed magnetic lines (gravity lines). Again repelling forces result from the contact of two quasi-definite energy-levels as an increase of magnetic quanta results at the contact. If it were possible to overcome the repelling forces the two bodies would unite in a new unit with a common quasi-definite energy-level. The positive and negative atomic charges would be a particular case of the general one mentioned. An electron, with decreasing density from the center, would establish a negative potential outward causing tiny radial currents with a dextrorotatory magnetic field. A proton formed by 1830 electrons would have two magnetic fields for each energy-level, one outside, dextrorotatory, and another, laevorotatory, inside. The latter for structural reasons would be larger and the difference for the whole energy-levels would be the positive magnetic mass μ which is 1/5 of the whole. $\mu=1/5\times2/3\times(5.5\times e^2\times10^4)/1.8\times10^{-9}\times c^2=2/3e^2/1.9\times10^{-13}c^2$ (electro-magnetic mass). The number of electrons of an average shell, with a radius of 1.8×10^{-9} cm, representing the proton, is $5.5\times e^2\times10^4$.

41. Measurement of electrical fluctuation phenomena. HAROLD A. WHEELER, Johns Hopkins University.—In experimental work on the "shot effect" and "flicker effect" in vacuum-tube amplifiers and on the "thermal agitation" in electric conductors, it has been customary to amplify and rectify the fluctuations, and to observe directly their mean square amplitudes. An alternative method of measurement has been developed in which the fluctuations are amplified and made to cause a proportional agitation of the indicator of a galvanometer. The average deviation of the indicator from its zero position is determined by a series of observations, and the mean square amplitude of the fluctuations is computed therefrom. This method is especially applicable to the measurement of fluctuation components within frequency bands less than one cycle wide, at audio or sub-audio frequencies. The flicker effect has been measured in two different amplifiers, in one case within a frequency band 0.4 cycle wide at 0.4 cycle resonant frequency, and in the other case within a frequency band 1.0 cycle wide at 150 cycles. These observations indicate that the flicker effect may be caused by disturbances of several seconds duration. The thermal agitation in a resistance of 10^7 ohms was measured by the latter amplifier; the agreement with the theoretical value was well within the probable error of the experimental value (8%).

42. A promising method for measuring x-ray intensities. R. T. DUFFORD AND H. E. HAMMOND, University of Missouri.—Three types of cells have been found which under influence of x-rays of average intensity give a photo-voltaic response of from 0.2 to above 0.8 volt; and on closed circuit give a current response considerably larger than could be obtained from ordinary ionization chambers. Certain of these cells reach the maximum response, and recover from it, in less than two seconds. The amount of the response is probably the largest on record for photo-voltaic cells. The voltage change appears to be approximately proportional to the logarithm of the x-ray intensity. Further study is in progress.

43. Polarization of cadmium resonance radiation 1^1S_0–2^3P_1 3261 A. A. ELLETT, University of Iowa.—This resonance line excited by plane polarized light is completely polarized in the absence of a magnetic field, and also in a field parallel to the electric vector of the exciting light. The radiation emitted in the direction of a magnetic field perpendicular to the exciting electric vector is rapidly depolarized with increase of the applied field, the observed points lying on the curve $P=1/(1+3640H^2)$, where $P=(I_x-I_y)/(I_x+I_y)$ I_x and I_y being the intensities of the radiation polarized respectively parallel and perpendicular to the exciting light vector. Both Eldridge and Breit have shown that the above relation is $P=1/([1+2(geH\tau/2mc)^2]$ so that τ, the mean life of the 2^3P_1 state of cadmium is 2.30 10^{-6} secs. Soleillet has recently given 0.92% as the polarization of this line in zero field. (C. R. Vol. **142**.) That this may be due to the depolarizing action of collisions is suggested by the fact that he likewise finds a smaller $\tau=2.0\times10^{-6}$ secs.

44. Reflection of atoms from crystals. A. ELLETT AND H. A. ZAHL, University of Iowa.—Cadmium and arsenic are diffusely reflected from crystals of flourite and orthoclase. A cadmium beam striking a KCl crystal gives rise to a distinct specular beam, but its intensity relative to that diffusely scattered is much less than in the case of Cd and NaCl crystals. Arsenic (As_4?) incident upon NaCl gives rise to a weak specular beam with much diffuse scattering. Arsenic deposited upon a glass surface at liquid air temperatures is transparent in layers of such thickness that when warmed to room temperature they transmit but 10 or 15% of the incident light. Very thick layers deposited at liquid air temperature are black. Such deposits as they warm to room temperature change very abruptly to a deep red—then a bright yellow, and finally to the usual steel grey modification.

45. Radiometer effect of positive ions. CHAS. T. KNIPP and WESLEY S. STEIN, University of Illinois.—Campbell Swinton concluded in 1907 that the rotation of a mica mill-wheel when bombarded by positive rays is also due to a secondary or radiometer effect, as Thomson theoretically, and Starke experimentally, had shown to be the case for cathode rays. Starke in his work with cathode rays eliminated the radiometer effect and got no rotation. In Swinton's work with positive rays this effect was present. In the present investigation with positive rays

the radiometer effect was eliminated by the method of Starke. The delicately suspended vane gave consistent deflections which corresponded to a *calculated* force of, $F_{calc.}=0.0017$ dyne. By measuring the positive ion current, and the potential difference impressed on the discharge tube, the corresponding *observed* force was, $F_{obs.}=0.0012$ dyne. Thus it seems that the speeding positive ions *do exert a measurable force.* Observations made with a lower potential and a lower vacuum gave, $F_{calc.}=0.0033$ dyne, and $F_{obs.}=0.0013$ dyne, respectively. The degree of exhaustion is a determining factor in the observed force.

46. Lenard ray tube having a glass window and adjustable gas pressure in the ray chamber. CHAS. T. KNIPP, University of Illinois.—In this tube the author has extended the technique of the construction of thin glass windows, described in *Nature*, **120**, 156 (1927), to meet the requirements for the production of Lenard rays. Thin walled hemispherical glass surfaces of diameters up to 2 and 3 cm and of any desired thickness can be readily and accurately blown. They are perfectly annealed by the manner of blowing and will withstand a surprisingly large outward pressure and yet be apparently vacuum tight. Tubes recently made operate readily on a 10 cm Max Kohl induction coil. The degree of exhaustion after careful baking being that of about 5 cm parallel gap in air. The range of the rays may be extended by reducing the "outside" gas pressure. By using a focus tube a compact beam may be had without the use of diaphragms. The beam may be made more luminous by priming with a suitable gas. These tubes and windows are made of Pyrex glass.

AUTHOR INDEX

Bartlett, James H. Jr.—No. 16
Bless, A. A.—No. 33
Boeckner, C. and F. L. Mohler—No. 24
Boyce, J. C.—see Compton
Brickwedde, F. G. and M. F. Peters—No. 12

Compton, K. T. and J. C. Boyce—No. 9
Condon, Edw. U.—No. 35
———— see Gurney

Davis, Harold T.—see Hufford
Davisson, C. J. and L. H. Germer—No. 21
Dershem, Elmer—No. 28
Dufford, R. T.—No. 26
———— **and H. E. Hammond**—No. 42
DuMond, Jesse—No. 39

Eldridge, John A.—No. 38
Ellett, A.—No. 43
———— **and H. F. Olson**—No. 22
———— **and H. A. Zahl**—No. 44
Elo, A. E.—see Monk
Erikson, Henry A.—No. 20

Gale, H. G. and G. S. Monk—No. 8
Germer, L. H.—see Davisson
Glockler, George—No. 13
Goeder, Frank P.—No.30
Gurney, Ronald W. and Edw. U. Condon—No. 36

Hammond, H. E.—see Dufford
Hull, Albert W.—No. 23
Hufford, Mason E. and Harold T. Davis—No. 10
Huxford, W. S.—see Williams

Johnson, Arthur J. M.—No. 27

Kaplan, Joseph and E. L. Kinsey—No. 6
Kimball, W. S.—No. 2
Kinsey, E. L.—see Kaplan
Knipp, Chas. T.—No. 46
———— **and Wesley S. Stein**—No. 45
Kunz, J. and J. T. Tykociner—No. 15

Langer, R. M.—No. 11
Lark-Horovitz, Karl—No. 31

Mohler, F. L.—see Boeckner
Monk, G. S. and A. E. Elo—No. 7
———— see Gale
Mortimore, Roy H.—No. 3

Olson, H. F.—see Ellett

Parsons, S. R.—No. 1
Peters, M. F.—see Brickwedde
Pool, M. L.—No. 17

Sagui, Cornelio L.—No. 40
Steadman, L. T.—No. 29
Stein, Wesley S.—see Knipp
Stewart, G. W.—No. 32

Tykociner, J. T.—see Kunz

Van Vleck, J. H.—No. 34

Walerstein, I.—No. 14
Wang, S. C.—No. 37
Wheeler, Harold A.—Nos. 5 and 41
Whitney, John D.—No. 18
Williams, N. H. and W. S. Huxford—No. 19
Woodrow, Jay W.—No. 25

Zahl, H. A.—see Ellett